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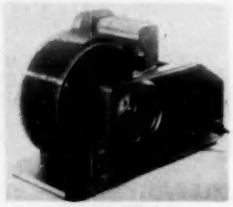

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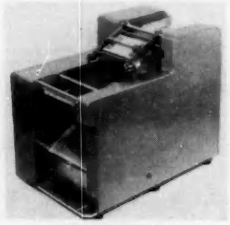

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The Surface of the Cotton Fiber

Part III: Effects of Modification on Soil Resistance

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Abstract

Experiments designed to complement microscopical studies and to attempt a practical evaluation of the effectiveness of various agents which impart resistance to dry soil are reported. Various methods of applying soil to fabric were evaluated, as was the effectiveness of a number of soil retardants. Soils included carbon blacks of a range of particle sizes, a natural clay, and a synthetic soil whose formula approximated the composition of natural soil, containing fatty materials. Fabrics were also soiled by foot traffic on the floor. Results were interpreted from reflectance data and from radioactive tracer assays of weight of soil takeup. In attempting to elucidate the mechanism of dry soiling, the effects of textile construction, electrical charge on the fiber, particle size of soil as related to topography of fiber surface, surface hardness, reducing surface roughness, and lowering surface energy were considered. It was shown that soil takeup is directly related to specific surface. It was found that grey cotton is slightly more resistant to soil than bleached cotton, and that increased smoothness of fiber, even to complete obliteration of native rugosities, did not necessarily impart soil resistance to cotton fabrics. The most successful types of antisoiling agents for dry soils appear to be colloidal particulate applications such as silica or alumina, and additive finishes which lower surface energy of the fiber. Only a few of the typical commercially available soil retardants were used in these studies. The project was a short term one and the experiments were designed for the study of the mechanism of soiling of cotton textiles which would be subject to in-place cleaning. Many new soil retardants were marketed after the experiments had been initiated.

Introduction

The problem of the soiling of cotton textile materials has become increasingly important with the more widespread use of cotton in items which require in-place cleaning. Floor carpeting and rugs are the most prominent examples. Other household uses, such as draperies, slipcovers, window shades, and industrial applications in automobile upholstery and awnings also represent end uses where cleaning by washing is not usually practical. As suggested in a recent publication by Getchell [6], the most realistic approach to this type of soiling problem is a study of the possibilities of soilproofing textiles

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before use. During the past few years, several types of additive finishes which impart soil resistance have become available. The finishes cover the fiber with materials which change the nature of the surface. Such finishes are not designed for a particular type of fiber and are reportedly about equally effective for all textile fibers [2, 24].

In attempting to understand the mechanism involved in the dry soiling of cotton, it was considered necessary to study the surface of the fibers in their native form and the changes in this surface caused by additive finishes or by chemical modification of the whole fiber. Study of the fiber surface by light and electron microscopical techniques made possible an examination of some physical mechanisms of soiling of the fiber. The results of these microscopical studies are reported in the other parts of this series of papers [25, 26, 27]. Experiments designed to complement the microscopical studies and to attempt a practical evaluation of the effectiveness of various agents as soil repellents are reported herein. It is hoped that by correlation of the two types of investigation, some of the mechanisms of the soiling process may be elucidated.

There exists extensive literature on the problem of the soiling of textile materials, but until recent years most investigations were concerned with detergent problems which utilized the techniques of wet soiling. Several reviews containing excellent literature surveys of the general problem of the soiling of textile materials have been published [6, 11, 16, 31]. Committee D-12 of the American Society for Testing Materials made a survey of the literature covering the redeposition of soil on cotton fibers and fabrics [1]. Effects of variation of fiber diameter on the extent of soiling have also been reported [20], and in the current literature are papers illustrating the antisoiling properties of some additive finishes now in commercial production [5, 19]. Reumuth [18], and Götte, Kling, and Mahl [8], in reports on investigations of the nature of the soiling process, included studies made with the techniques of electron microscopy. The experimental procedures reported in this paper were designed after consideration of the various methods used in these reports.

TABLE I. Treatments and Modifications of Cotton Fabrics Used in Soil Resistance Studies

Treatment or modification	Remarks
Chemical modification:	
Partial acetylation	Varying acetyl contents up to 25% [7]
Partial carboxymethylation	Degree of substitution approximately 0.1 [3]
Cyanoethylation	Etherified with acrylonitrile. Nitrogen content 4.0% [4]
Methylolmelamine creaseproofing agent	8.2% add-on [15]
Amine-decrystallization	Immersed in pure ethylamine for 12 hr. 60% crystallinity [22]
Mercerization	Slack mercerization and mercerization with tension included
Additive finishes:	
A. Film Formers:	
Starch	2–3% add-on
Carboxymethyl cellulose	Low viscosity CMC, 2–4% add-on
Chrome complex of perfluorooctanoic acid	0.1–2.0% add-on of chromium
Dialkyl ketene	A water-repellent finish 2% add-on
Silicone water-repellent finish	2% add-on
Perfluorodecanoic acid	Applied from saturated n-hexane solution; 0.2% add-on [28]
Soft acrylic polymer dispersion	25% add-on
B. Particulate Dispersions:	
Colloidal silica	Particle sizes 17, 30, or 63 mμ (average); 2–7% add-on
Hard acrylic resin dispersion	5% add-on
Colloidal silica-alumina	2–7% add-on [24]
Polytetrafluoroethylene dispersion	5% add-on

Materials and Methods

Test Fabrics

All additive finishes were applied to a basic test fabric from a single bolt of 80-square cotton print cloth obtained from a commercial mill. This material had been singed and desized; about one-half of the bolt had been peroxide-bleached and a portion of the bleached fabric had been mercerized by a commercial process. Chemically modified fabrics were obtained from lots treated in this laboratory. The treatments and modifications studied are listed in Table I.

The chemically modified fabrics varied in some cases from an 80-square construction, but thread counts were not widely different. Differences in soiling resistance between untreated fabrics with widely different thread counts were found to be of

a lower order than differences imparted by soil-resistant finishes or treatments.

For investigations of varietal differences in soil resistance, samples of roving made from several different varieties of cotton were used. In addition, yarns of synthetic fibers and of mercerized cotton were compared in a single series of soiling experiments.

Soils

The variety of soils observed in studies of soiling response is described in Table II. The carbon blacks were selected for studies of soil particle size effects because they were available in lots of known mean particle size and were a true black in color. The synthetic soil was designed to simulate a natural soil and contained an oil. The use of the synthetic soil, the clay, and the test by floor soiling served to emphasize the practical evaluation of the soil-resistant agents being studied microscopically [25, 26].

TABLE II. Types of Soils Used in Soiling Experiments

Soil	Particle size (Average)	Remarks
Carbon blacks*		
Carbolac 1, 83% fixed carbon	90 Ångstroms	All obtained from the Godfrey L. Cabot Co., Boston, Mass.
Monarch 81, 95% fixed carbon	220 "	
Sterling 99R, 99% fixed carbon	450 "	
Sterling R, 99% fixed carbon	800 "	
Nuchar*	greater than 1000 Ångstroms	Decolorizing charcoal
Clay	Unknown, but large	Ceramic clay
Synthetic soil†	Mixed	
Floor soil	Mixed	Third floor office areas and basement shop areas of the laboratory

* It is not the policy of the Department of Agriculture to endorse the products of one manufacturer over similar products of other manufacturers; names are used for convenience in designation.

† Ingredients of the synthetic soil were peat moss (38%), cement (17%), clay (17%), silica (17%), Molacco furnace black (1.75%), red iron oxide (0.5%), and mineral oil (8.75%). This is the soil described by Salsbury *et al.* [19].

Soiling Equipment and Methods

Several different soiling procedures were used in these experiments. In each case the method was designed to accommodate the particular soil and material being studied. No attempts were made to simulate in any manner a final production test and the overall testing efficiency of any single technique was not evaluated.

Soiling of a Charged Fabric

A few experiments were conducted to determine the difference in the extent of soiling of electrically charged and uncharged fabrics. One sample was clamped in a metal embroidery hoop whose potential could be varied from 0 to + 1500 volts. An uncharged control sample was similarly mounted in a wooden hoop and the pair were clamped to opposite sides of a wooden box lined with aluminum foil. The selected soils were sprayed in through a hole in the hinged plastic cover and allowed to settle by gravity. The rate of dispersion and the quantity of soil used were not constant and a control sample was necessary in each trial.

Soiling by Airborne Soils

These trials were designed to illustrate soiling of vertically suspended fabric by airborne soil. Only a few trials were conducted because the impinged soil was easily removed by vacuuming. Samples held in embroidery hoops were suspended from each of the four sides of the box described above and the selected soil sprayed in. This technique proved inefficient as large quantities of soil were needed to produce detectable changes in the reflectance of the fabrics and it was necessary to use a control with each set of three samples tested.

Tumbler Soiling

The colloidal carbons were applied to the test fabrics by tumbling 3 in. square samples of fabric in a 1 qt. size tin can with 1–2 g. of the selected carbon black and about 50 ml. of small glass beads. The can, closed with a friction type lid, was mounted on a paddle and rotated through a fixed eccentric orbit for 15 min. at the rate of 50 rpm. These test conditions produced saturation soiling of the samples.

The same equipment was used in the soiling of yarns of cotton and of synthetic fibers and rovings

fabricated from single varieties of cottons. In these tests the rovings were weighed, made into bundles approximately 3 in. in length, and tied in the center. Previously measured aliquots of labeled soils were used, and the quantity of glass beads was increased to 100 ml. A plastic jar was used instead of a tin container.

Rotating Soiling Cylinder

In order to secure a more controlled soiling at less than saturation level with synthetic soil, a soiling cylinder similar in principle of operation to those described by other investigators [5, 19] was fabricated. The weighed soil loads were contained in a concentric cylinder designed to sift the soil onto the four radially mounted fabric samples. About 50 ml. of glass beads were used to rub the soil into the samples. The cylinder was rotated at about 30 rpm in one direction for 5 min.; another soil load was added and the cylinder then rotated in the opposite direction for 5 min. The quantity of soil used in each loading was determined by the particular test being conducted. The extent of soiling was easily controlled by this method of application and control fabric samples were needed only when another parameter was varied.

Floor Soiling

The sample squares to be tested were sewn together and backed with $\frac{1}{16}$ in. cardboard. This assembly was then stapled to a rubber mat of an appropriate size. The rug was placed in passageways, either in the third floor offices or in the mechanical shops area in the basement of the laboratory building. At desired intervals the rug was vacummed, the fabric samples removed, and reflectance measurements made. Untreated control samples were used in each rug because no measurements were made of the total traffic.

Methods of Measurement of Soil Retention

The problems of evaluation of the soiling of fabrics and the need for some standardized techniques were recognized from the review of the extensive literature on this subject [9, 11, 13, 17, 19, 29, 30].

In our experiments fabric samples were routinely cleaned with the upholstery attachment of a tank type vacuum cleaner, using three passes in one direction and three in a perpendicular direction. Further vacuuming produced no decrease in soil retained by the fabric. In some cases, samples were brushed or shaken, but final comparisons were made with vacuumed samples. The yarn and roving samples were cleaned by placing the soiled bundles in a covered well over the screened outlet of the upholstery attachment and turning on the vacuum for 5 min.

Reflectance measurements were made with a Hunter Multipurpose Reflectometer, equipped with tristimulus filters [12]. This instrument was calibrated for 100% reflectance with a freshly prepared magnesium oxide surface and for the entire reflectance scale with a set of standard plaques procured from the National Bureau of Standards. Single sample thicknesses were used throughout, backed with several sheets of filter paper. Reflectance readings made in each of two perpendicular directions on the fabric samples failed to show any significant differences in the readings for the fabrics or soiling procedures used in this study. A minimum of four samples of each fabric and fabric modification was used in each experiment.

For a few soiling tests Strontium 89, a radioactive isotope, was used to label synthetic soil, Nuchar, and clay. The Nuchar and clay were directly labelled by immersion in an aqueous solution of $SrCl_2$; the synthetic soil was labeled by mixing 0.1 g. of labeled Nuchar with 25 g. of soil. Conventional radioactive assay techniques were used to measure the soil retained by the fabric or yarn samples. The counting rates of the soiled samples were compared to those of calibrated fabric samples in order to convert the counting rates to grams of soil. The tracer technique was used principally to validate the method used to interpret the reflectance readings.

Changes in reflectance readings caused by soiling of the sample surface may be linearly related to the quantity of soil producing the change by use of the Kubelka-Munk equation, which was developed for this purpose [10]. This equation is expressed as

$$\frac{(1 - R_s)^2}{2R_s} - \frac{(1 - R_c)^2}{2R_c} = kW_s \qquad (1)$$

where R_c is the reflectance of the unsoiled sample, R_s, the reflectance of the soiled sample, W_s, the weight of soil, and k, a constant of proportionality. In the soiling tests reported in this paper, it was not possible to adhere rigorously to the conditions for which the equation was developed, but results could

be confirmed by radioactive tracer techniques. When the weight of synthetic soil retained was measured by use of Strontium 89, the values obtained were seen to bear an approximately linear relationship to the weights determined on the same samples by the Kubelka-Munk interpretation of the reflectance readings on the same samples (Figure 1).

In reporting the data, the product kW_s in Equation 1 is referred to as the Kubelka-Munk Index (KMI). The value of the index increases with increased soiling. In some instances the data are expressed as the Kubelka-Munk Index ratio (KMI ratio) and represent the ratio of the KMI of a treated sample to that of an untreated sample. Thus, a ratio of less than one represents increased soil resistance; a ratio greater than one, a decrease in soil resistance.

The problem of soiling of colored fabrics was tentatively investigated by soiling various colored Indian Head samples with the labeled soil and making simultaneous reflectance and radioactive measurements. As might be expected in the case of colored materials, the interpretations of reflectance measurements designed for use with white and near white materials did not agree with the measurements of the amount of labeled soil retained on the fabric. A similar discrepancy was observed when comparing soil takeup values for tan colored clay on white fabrics. Further investigations of the color problem were beyond the scope of this study.

Results

Soiling with Carbon Blacks and Charcoals

Typical results of saturated soiling with the carbon blacks, a wood charcoal, and an animal charcoal are illustrated in Figure 2. The values denoted as functions of the weight of retained soil were corrected to compensate for variations in weight of soil load in the tumbler. Data from experiments on bleached 80-square fabric only are illustrated, but a similar relationship was observed for unbleached and for mercerized fabrics. The protective effect of a commercial antisoiling agent, a colloidal silica-alumina, is demonstrated in the lowest curve. Electron micrographs of surfaces of fibers soiled with the carbon blacks showed the particles tended to agglomerate, thus probably diminishing the particle size effect.

The effects of variation in the size of the colloidal particles in a silica retardant are shown in Table III.

TABLE III. Soil Resistance of Treated Bleached Fabric as a Function of the Particle Size of a Colloidal Silica Soil Repellent *

Average silica particle size (Å)	Kubelka-Munk Index ratios			
	Sterling 99R (450 Å)	Nuchar (2000 Å)	Synthetic soil (mixed)	Floor soil (mixed)
170	0.06	0.20	0.74	0.33
300	0.23	0.46	0.73	0.26
630	0.44	0.58	0.97	0.37

* Dry add-ons of 2% were used except in the floor soiling tests, in which 7% add-ons were used.

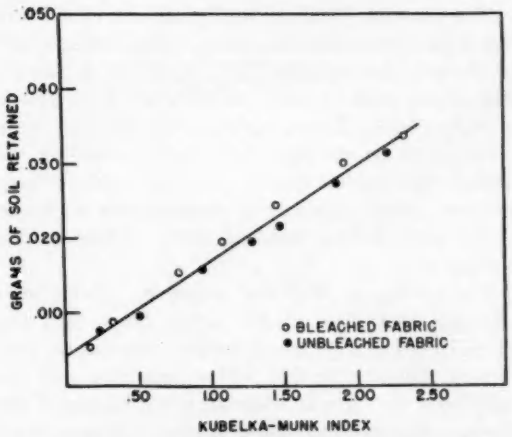

Fig. 1. Relation of Kubelka-Munk Index to weight of synthetic soil retained by 80-square fabric after vacuum cleaning.

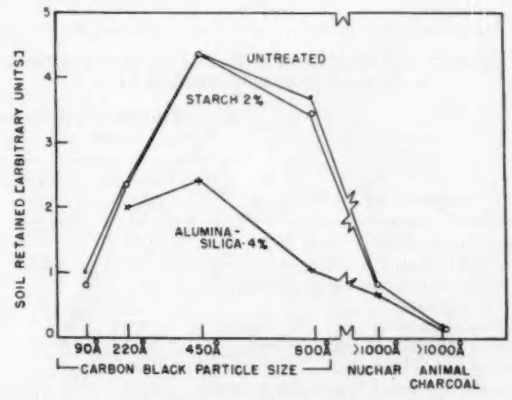

Fig. 2. Extent of soiling of untreated and treated samples of 80-square fabric with carbon soils of varying particle size.

Retardant effects are seen to be a function of the particle size of the soil tested. The same order of soil resistance was observed for similarly treated unbleached fabric, with the exception of the floor soiling test, in which 300 Å silica appeared even more effective. More protection is secured against soiling with the particulate soils, Sterling 99 R and Nuchar, by the smaller sized retardant particles than by the coarser ones, although the degree of distinction observed for the synthetic soil or for floor soil is much less. The carbon black used in the synthetic soil has an average particle size of 800 Å, but comprises only 1.75% by weight of the soil mixture. The carbon black content of the floor soil was unknown.

The charcoal, Nuchar, was used in tumbler soiling tests because it was most easily distinguished in electron micrographs [27] from the particulate dispersions used as soil retardants by the irregular particle shape. These particulate dispersions were observed to be the most effective in retarding the soiling with Nuchar (Table IV). The film forming additive agents appeared to decrease the resistance of the untreated or bleached fabric surface to this type of soil.

The soiling of vertically suspended fabrics with airborne dispersions of the carbon blacks was not extensively investigated, as the few experiments performed showed that this soiling technique was not sufficiently sensitive to illustrate the efficiency of the various dry soil retardants studied. Experiments with charged fabrics, under the same conditions, were also few in number, as this variation of the technique failed to yield pertinent information. At a potential of 1000 volts, grey, bleached, and mercerized fabrics collected approximately three times as much soil as the uncharged fabric when exposed to soils for 40 min. The increase in soiling of the charged fabrics was observed to be a function of the time of exposure; the type of carbon black or charcoal used had no observable effect. At potentials of less than 1000 volts, smaller differences in the soiling of charged and uncharged fabrics were observed. In the experiments with uncharged fabrics, only a slight resistance to soiling with Nuchar was observed for 2% dry pick-ups of carboxymethyl cellulose and a colloidal alumina and silica compound. When screened vacuum cleaner sweepings from a surburban residence were used, no detectable change in reflectance was noted after vacuuming the samples.

Perhaps the most significant finding of the experiments with airborne dispersions of carbon blacks was the very obvious heavy soiling of the loose fibers protruding from the surfaces of the yarns. This appeared to be the first step in the soiling of vertically suspended fabrics and suggests that any retardant which tends to reduce the number of such loose fibers will afford some degree of soil protection.

TABLE IV. Soil Resistance of Treated and Modified Fabric to Charcoal (Nuchar) in Tumbler Tests

Treatment or modification	Kubelka-Munk Index ratios	
	Bleached fabric	Grey fabric
Acetylated colloidal silica, 2% add-on	.30	
Colloidal silica, 2% add-on	.39	.33
Acetylated colloidal silica-alumina, 2% add-on	.85	
Colloidal silica-alumina, 2% add-on	.91	.83
Methylolmelamine creaseproofing	1.03	
Acetylated, 25% acetyl	1.07	
Cyanoethylated, 3% nitrogen content	1.11	
Slack mercerized	1.27	1.17
Dialkyl ketene, 2% add-on	1.47	1.40
Silicone water repellent, 2% add-on	3.51	

Soiling with Synthetic Soil

Soil resistance data obtained when treated samples were soiled by a single application of 0.125 g. synthetic soil/sample in the soiling cylinder are given in Table V. Continuous incremental soiling of fabrics treated with three of the agents judged most soil resistant from the data in Table V was carried out. In these continuous soiling tests each reading was taken after the application of only 0.05 g. of soil. From these data, which are graphed in Figure 3, it appears that particulate dispersions vary in their resistance to removal of the protecting particles by abrasion with glass beads or by vacuuming.

Floor Soiling

A series of rugs composed of samples of the treatments and modifications under study were placed in office passageways and in the mechanical shops area. The results obtained depended to some extent on the nature of the foot traffic. The office areas were on the third floor of the building and were not exposed to heavy traffic or to traffic freshly contaminated with outdoor soil. In the shops areas in the base-

ment, on the other hand, the traffic was heavy and predominantly male, with resulting increase in impact pressures. Moreover, the soil carried by the foot traffic was darker in color and contained more greasy components.

No significant soiling resistance was found in any of the floor soiling tests for samples of carboxymethylated or cyanoethylated fabric or for samples of bleached and unbleached fabric treated with starch or carboxymethyl cellulose. Both samples treated with the silicone water repellent finish and samples of decrystallized fabric showed an increased soiling. Some resistance to soiling was shown by mercerized samples, but this was neither large nor consistent. Samples of acetylated fabric appeared resistant to soiling in the office areas, but tests in the shops areas failed to confirm this resistance. It is thought that this failure was caused by the larger amount of grease in the shops soil. Very little soil resistance was found for fabrics containing less than about 20% acetyl.

The results of a typical floor soiling test in the office area are plotted in Figure 4. The Kubelka-Munk Index values were obtained from the reflectance readings made at intervals of 4, 7, 10, 16, 22, 32, 40, and 51 da. on the vacuumed samples. Marked differences in extent of soiling of the variously treated samples began to appear after about 10 da. All acetylated samples showed the soil resistant characteristics mentioned above. The soiling rates of the treated acetylated samples began to decrease at about 10 da. and appeared to level off as seen in Curves 1 and 2. Similarly, the rate of soiling appeared to decrease for samples of bleached and unbleached fabric treated with colloidal silica-alumina and with methylolmelamine, as seen in Curves 4, 5, and 6. These samples showed, under the specific conditions of this test on the office floor, more total soiling than was evidenced by the treated acetylated fabrics of Curves 1 and 2.

TABLE V. Soil Resistance of Treated and Modified Fabric to Synthetic Soil in Soiling Cylinder Tests *

Treatment or modification	Kubelka-Munk Index ratios: Bleached fabric	Kubelka-Munk Index ratios: Grey fabric
Perfluorodecanoic acid, 0.2% in n-hexane	.10	.52
Hard acrylic resin dispersion, 5% add-on	.16	.39
Mercerized colloidal silica, 7% add-on	.23	
Colloidal silica-alumina, 7% add-on	.25	.31
Colloidal silica, 7% add-on	.26	
Acetylated colloidal silica, 2% add-on	.38	
Dialkyl ketene, 2% add-on	.41	1.28
Acetylated colloidal silica-alumina, 2% add-on	.41	
Silicone water repellent finish, 2% add-on	.44	.94
Methylolmelamine creaseproofing agent, 8.2% add-on	.60	
Carboxymethyl cellulose, 2% add-on	.71	1.50
Commercial mercerization	.74	
Polytetrafluoroethylene dispersion, 5% add-on	1.97	1.69
Starch, 2% add-on	.98	1.31
Cyanoethylated, 4.5% nitrogen content	1.01	
Decrystallized, 60% crystallinity	1.03	
Slack mercerized	1.34	1.34

* Soil was applied in single applications of 0.125 g./sample.

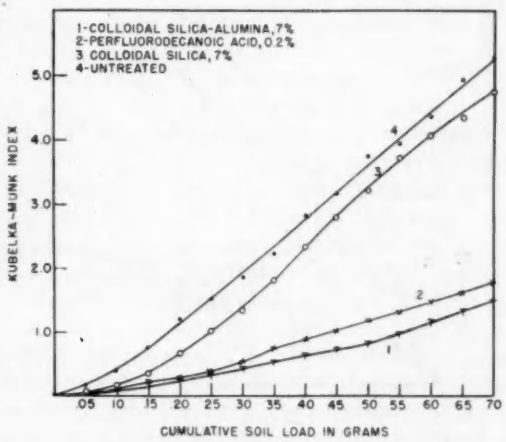

Fig. 3. Continuous incremental soiling of treated and untreated bleached 80-square fabric with synthetic soil.

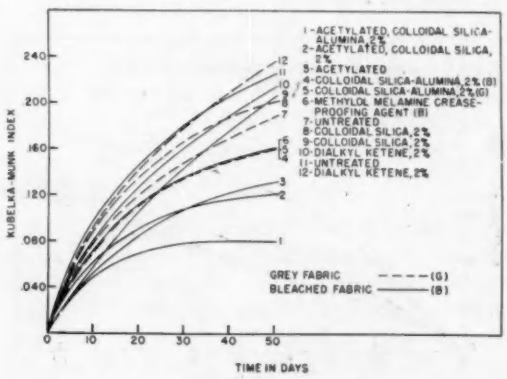

Fig. 4. Extent of soiling of untreated and treated grey and bleached 80-square fabric by foot traffic in office passageways.

The increase in soil resistance obtained by increasing the dry add-on of two of the particulate dispersions from 2 to 7% is illustrated by the data plotted in Figure 5. These data were calculated from the reflectance measurements made on a rug placed in the shops area; the darker and heavier soiling in this area is indicated by the larger indices obtained in shorter exposure times compared to the coordinates of Figure 4. Marked improvement in soiling resistance is shown by the samples treated with the 7% applications of the retardants. The soil resistance of another particulate-dispersion type of retardant, a hard acrylic resin dispersion, and of fabric treated with perfluorodecanoic acid was about equivalent to the resistance obtained by using a colloidal silica-alumina (Figure 6) under the rigorous soiling conditions of the shops area. From the practical viewpoint, these three methods of retarding dry soiling appear to be equally effective. However, the mechanism of soil prevention cannot be identical for the three agents. The only point of similarity between them is the retention of the particulate nature of the colloidal silica-alumina and the hard acrylic resin dispersion after application to the fiber. This characteristic is not held by the perfluorodecanoic acid treatment.

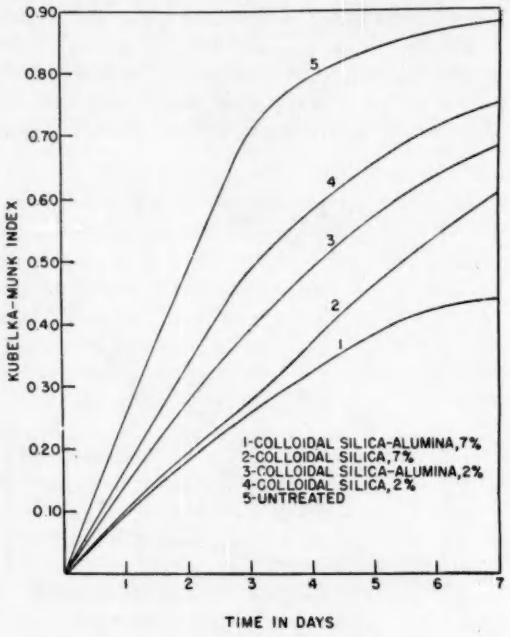

Fig. 5. Extent of soiling by foot traffic in mechanical shops area of 80-square fabric untreated and treated with particulate soil retardants.

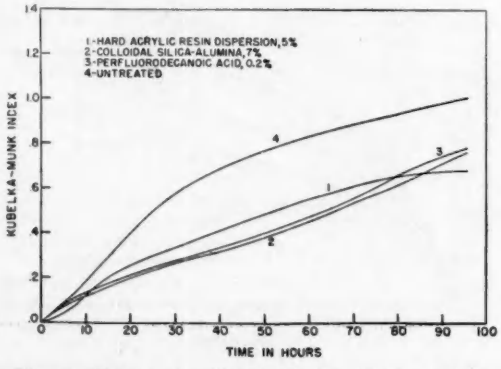

Fig. 6. Extent of soiling by foot traffic in mechanical shops area of bleached 80-square fabric, untreated and treated with various soil-retardant finishes.

Soiling with Clay Labeled with Strontium 89

A few representative modified fabric samples were soiled with clay labeled with radioactive strontium. This clay was a ceramic type and proved difficult to use because it was quite dusty, consequently more hazardous to handle than either the labeled synthetic soil or Nuchar. The soiling cylinder was used to apply single loads of 0.125 g./sample for a total soiling time of 20 min. using 100 ml. of mixed-sized glass beads to rub in the soil. The results are expressed as the ratios of the grams of soil retained by each sample listed to the grams retained by untreated bleached fabric (Table VI).

Varietal Differences in Soiling

Rovings of different varieties of cottons were made available for soiling tests. These were soiled both with labeled Nuchar and with the labeled synthetic soil to determine varietal differences in soiling

TABLE VI. Soil Resistance of Treated and Modified Fabric to a Sr^{89}-Labeled Ceramic Clay in Soiling Cylinder Tests

Treatment or modification	Weight ratio (treated/ untreated)
Colloidal silica-alumina, 7% add-on	0.59
Commercial mercerization	0.65
Acetylated	0.65
Grey, untreated	0.76
Carboxymethyl cellulose, 2% dry pick-up	0.88
Silicone water repellent finish, 2% add-on	1.00

properties. Weight fineness of the cottons had been determined by the Suter-Webb method in this laboratory. These data were used to give a relative surface area per microgram of the cottons, using the surface area of the Iquitos variety as 1.00. The relative number of ridges per micron of surface perimeter was derived from data obtained from electron micrographs of the fiber surface [25]. These measurements are given with the soil resistance data in Table VII. The soiling data appear to correlate with the relative surface area per microgram and do not appear to be significantly related to the number of ridges per micron of surface perimeter.

Comparison of the Soiling of Cotton and Synthetic Yarns

Labeled synthetic soil was also used to compare the soil resistance of cotton to that of some of the synthetic fibers. Yarns of mercerized cotton, nylon, Dacron,[2] acetate and viscose rayons, and glass fibers obtained from commercial sources were used. Identical lengths of yarns were used and soil takeup values were all corrected to the same yarn perimeter value. Soil retention was found to be lowest for nylon and increasingly higher for cotton, Dacron, acetate rayon, viscose rayon, and glass fibers in that order. Appearance values would not necessarily follow the same ordering. No reflectance measurements were made in these exploratory experiments because actual soil takeup values were considered more informative for studies of soiling mechanisms. None of the yarns were extracted before testing; the soil takeup values may have reflected the effects of surface coatings used during processing. However, the relative soil takeup values by this radioactive tracer technique were found to be the same as those reported by Weatherburn and Bayley [31], who extracted their samples before soiling and measured extent of soiling colorimetrically on dissolved aliquots of the fibers. They found that visual appearance is not necessarily indicative of soil content for all fibers.

TABLE VII. Soil Resistance of Rovings of Different Varieties of Cotton to Sr^{89}-Labeled Wood Charcoal and Synthetic Soil

Variety	Relative surface area/ mmg.	Relative soiling with Nuchar*	Relative soiling with synthetic soil	Number of ridges/μ of perimeter
Iquitos	1.0	1.0	1.0	No data
Rowden, raingrown	1.4	1.9	1.0	1.9
Deltapine, raingrown	1.7	2.4	1.1	2.2
Deltapine, irrigated	1.8	2.2	1.4	2.6
Acala, irrigated	2.3	2.8	1.4	2.1
Egyptian Karnak	2.9	3.2	1.5	2.0

* Relative soiling values were calculated by taking the ratio of the counting rates of each variety to the counting rate of Iquitos cotton.

Results of the Use of Fluorochemicals as Soil Resistant Agents

Evaluation of the soil resistance of fabrics treated with the chrome complex of perfluorooctanoic acid [14] (Table I) has not been included in the tables of soiling data given above because this compound imparted a green color to the test fabrics. The depth of the color increased markedly with increased dry add-on. There was visual evidence of increased soil resistance under all conditions of test and this evidence was visually confirmed in tests with a control fabric dyed to match the color of the treated samples. Further confirmation of the soil resistance of treated samples was obtained when these samples were soiled with labeled synthetic soil. On samples of bleached fabric treated with the chrome complex, the ratios of the soil retained by the treated sample to that retained by the untreated samples were 0.49 and 0.43 for dry add-ons of 0.05% and 2.0%, respectively; and for unbleached fabric, 0.78 and 0.61 for dry add-ons of 0.1% and 2.0%.

The same mechanism of soil resistance is illustrated by the application of perfluorodecanoic acid (Table I and Figure 6), which did not change the color of the test fabric [28].

Discussion

Evaluation of Soil Resistance

For truly rigorous investigation of soiling mechanisms, the quantity of soil retained by the fiber surface was considered to be more important than changes in fabric appearance. Appearance changes have been found to be influenced by fabric construction and fabric color, either of which masked fiber surface conditions. If the quantity of soil retained

[2] Registered trademark for du Pont's polyester fiber.

Fig. 7. Photomicrograph of fabric surface showing soiled fuzz fibers lying above the plane of the fabric. Magnification 30 ×.

were known and could be separated from fabric binding effects, soil resistance should be the same for the fiber under all conditions of manufacture. It was for these reasons that a basic 80-square fabric was chosen for this series of experiments and that attempts were made to keep the soil and fabric color within the range of experimental conditions imposed by use of the Kubelka-Munk equation.

Mechanism of Dry Soiling

Effects of textile construction. Although the effects of fabric and yarn construction on soiling should be obvious, it is necessary to consider them. Figures 7 and 8 show two important effects. The most dramatic is the soiling of the fuzz fibers which protrude from the surface of the yarns (Figure 7). These surface hairs become heavily soiled in nonabrasive soil applications and are a large factor in the soiling of any fabric containing such loose fibers. This soiling is caused by the large increase in the surface area available. Any treatment which reduces available surface will impart some measure of soil resistance to the fabric. It seems probable that part of the success of certain soil retardants now applied to textiles is the result of reduction in exposed surface area of the fibers. In Figure 8 the formation of soiling sites in the corners produced at the crossover points of the yarns is illustrated. The soil between yarns may be removed efficiently by vacuuming, but agglomerations of soil form in the corners and tend to grow during subsequent exposure. A series of optical photomicrographs taken during the incremental soiling experiments with synthetic soil showed this effect on both treated and untreated fabric.

The entrapment of soil between fibers in a yarn was routinely observed in microscopical examination of soiled materials. These soiling sites are made available by loose yarn constructions and by spreading of the yarns under pressure during impact soiling. Treatments which seal off interfiber spaces in the yarn may be expected to impart some measure of soil resistance. Varietal differences in soiling of cotton fibers which seemed to correlate with relative surface area per microgram (Table VII) probably have no practical significance in commerce because differences characteristic of coarse or fine varieties would be masked by the complexities of yarn and fabric construction. The data of Table VII merely imply that total surface area is more important than fiber surface rugosity.

Effects of electrical charge. The data from the tests made at the particular voltages used showed that a charged fabric collects more soil than an uncharged one. The practical results of this mechanism of soiling are probably not very important in most end use conditions for the cotton fiber. A measurable charge could be induced by friction, as indicated in a few trials in which an ebony rod was used to rub some cotton fabric samples and the samples then laid on the support of a gold leaf electroscope. Most of the samples were quite easily discharged by casual contact, or the charge leaked off quite rapidly. One modified fabric, acetylated cotton, was shown to retain a large charge for long periods of time. However, this finish proved fairly resistant to all but greasy soils. The synthetic fibers are known to become and remain charged; the use of antistatic finishing agents is an accepted practice in textile manufacture for these fibers. Here also the effect of charge on soiling was a contradictory one, for in the yarn soiling experiments, nylon, recognized as one of the most easily charged of the synthetic fibers, showed the least soil takeup of all of the fibers considered.

Effects of soil particle size. The relationship of soil particle size and extent of soiling was investigated by means of carbon blacks whose particle

sizes were known. The data illustrated in Figure 2 indicate that carbon blacks in the 220 Å to 800 Å range soil the most. Maximum soiling was obtained at the 450 Å particle size, the minimum at 90 Å. Both the charcoals, whose average particle sizes were greater than 1000 Å, also showed a relatively low soiling ability. Although it would be tempting to try to relate this particle size effect to the average depth and width of the rugosities on the fiber surface, both of which were found to be 5000 Å [23], soiling of the tumbler, the glass beads, and other surfaces by the 450 Å black was observed visually to correlate with the intensive soiling of the fabrics under test. The differences in soiling power do not correlate with the fixed carbon content of the blacks, as shown in Table II, but are more likely to be related to differences in surface properties. Similar differences in surface properties of carbon blacks have been encountered in studies of pigments [23]. The tendency of the particles to agglomerate into large clumps may also distort the effects of average particle size.

Another view of particle size effect is had from the data of Table III, which shows soil resistance as a function of the particle size of the repellent. The colloidal silica tested may be considered to be white dirt and to occupy the soiling sites available, thus preventing adherence of the carbon particles. Repellency toward the 450 Å carbon black was not only the most efficient but also the most sensitive to the particle size of the silica repellent. The 170 Å silica gave approximately seven times the repellency of that found using a 630 Å silica; less sensitivity to silica particle size was obtained for the larger carbon blacks and charcoals. No definite trends were seen for synthetic and floor soiling.

Effects of reducing surface roughness. Many of the treatments and modifications used in this study noticeably altered the surface topography of the fiber [26]. Bleaching and mercerization increased the average distances between ridges on the surface. Mercerizing also eliminated the microfibrillar network of the primary wall, which was uncovered in scouring processes. Applications of starch and of carboxymethyl cellulose appeared to form films, which smoothed the ridges somewhat but left the contours essentially unchanged. The silicones and the soft acrylic polymer studied formed entirely new surfaces, which were smooth continuous films covering the fiber surface and obliterating all trace of the corrugations. None of these treatments, however, resulted in significant improvements in soiling resistance.

Several agents did produce a change in soiling characteristics accompanying the change in surface roughness. Acetylation was seen to produce a scarring and smoothing effect of the fiber surface with obliteration of the ridges and of the fibrillate nature of the outer wall. This modification was found to be significantly soil resistant under certain soiling conditions. However, other chemical modifications, such as cyanoethylation and carboxymethylation, which resulted in a similar smoothing of the fiber surface, failed to produce significant soil resistance.

Agents such as the colloidal silicas and the hard acrylic resin dispersion, which produced a change in surface roughness by filling up the grooves but did not completely obliterate the contours, gave significant soil resistance in even the 2% dry add-ons. Higher concentrations of the colloidal silicas (7% dry add-ons) obliterated the native contours, producing an entirely new surface with a characteristic roughness peculiar to that finish; maximum soil resistance resulted from such a treatment. Thus it appears that smoothness alone is not a primary quality for soil resistance; other surface characteristics must be considered.

Effects of lowering surface energy. Two of the most soil resistant treatments, perfluorodecanoic

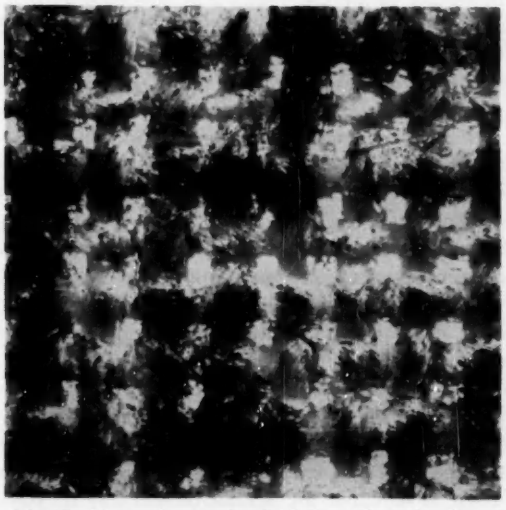

Fig. 8. Photomicrograph of fabric surface showing occlusion of soil in corners at yarn interstices after vacuum cleaning. Magnification 10 ×.

acid [28] and the chrome complex of perfluorooctanoic acid [14] produced little change in the electron microscopic appearance of the fiber surface, although they gave a soiling resistance comparable to that shown by the higher add-ons of the particulate type materials. These fluorocarbon agents produce a very low energy surface which is especially effective against the oily components of the soils [21]. This property of surface energy, which could not be evaluated by microscopical techniques, appeared to be a very important mechanism. Oil repellency is an outstanding characteristic of low energy surfaces such as those produced by the oriented fluorinated hydrocarbon chains [14]. Since fluorine is the most electronegative of the elements, the decrease in surface energy available for bonding is most marked for this element. Less electronegative elements probably do not decrease the surface energy sufficiently to be of value in this respect.

Effects of surface hardness. As there was no method for obtaining a physical measure of even relative surface hardness of the finishing agents or of the native fiber studied in this series of papers, hardness will be qualitatively described by the appearance of the agent on the fiber surface. Needless to say, such definition is peculiar to the conditions of this particular study. Any colloidal finishing agent which was observed in the electron micrographs to maintain its particulate integrity after application to the fiber surface is described as hard. The colloidal silicas and aluminas and the hard acrylic resin dispersions were seen in the electron micrographs [26] to remain on the treated fibers as discrete particles, filling the grooves on the surfaces at low concentrations, then forming close-packed but visually still particulate aggregates at higher concentrations. Fiber surface contour was not necessarily radically altered to produce this condition of hardness. In contrast, the soft acrylic polymer apparently coalesced on the fiber surface, forming a film which obliterated the topographical detail of the untreated fiber. Micrographs of fiber surfaces treated with a silicone water repellent finish also showed this film formation and obliteration of surface detail. Large increases in soil resistance were obtained when agents described as hard were used, as may be seen by examining the data in Tables I–V, while the agents of the soft or film-forming type failed to show much increase in soil resistance, and caused marked increase in soiling in some cases.

Conclusions

While many of the observations reported in this paper are not quantitative, certain general conclusions can be drawn from the qualitative information accumulated. In summary, the following points may be emphasized:

1. Measurements of soil pick-up by radioactive tracer techniques have shown that the Kubelka-Munk reflectance functions give valid estimates of the relative amounts of soil present on white fabrics.

2. In comparisons of the soiling tendency of different cottons it was found that soil pick-up is directly related to specific surface (*i.e.*, coarse cottons soil to a lesser degree than fine cottons).

3. Untreated (grey) cotton was found to be slightly more resistant to soil than bleached cotton. This is presumed to be due to the rougher surface (at the submicroscopic level) of the primary wall skeleton, a network of fine fibrils exposed by removal of waxy and pectinaceous material during scouring and bleaching.

4. In the evaluation of soil resistant treatments it was found that increased smoothness of fiber surface topography and even complete obliteration of native rugosities did not necessarily impart soil resistance to cotton fabrics. The most successful anti-soiling agents for dry soils appear to be colloidal particulate applications such as silica or alumina, and additive finishes or chemical modifications which lower surface energy of fiber surface.

5. Laboratory experiments on fabrics treated with certain particulate soil retardants have shown that the efficacy of these materials decreases with usage, presumably due to physical removal of the agent.

6. The effect of hardness of particles or of surface could not be evaluated directly, but it was noticeable that particulate emulsions which retained their particulate nature were more effective than emulsions, the particles of which merged to form a continuous film on drying.

7. Soiling studies indicated that additive finishes, such as some of the acrylic resins which create a soft fiber surface, increase the soiling tendency of the fabric.

8. A soil resistant treatment which reduces surface energy has been investigated for rendering cotton resistant to greasy soils. The soil resistance achieved is equivalent to that of the colloidal particulate type of soil retardant, but the mechanism of soil retardancy is believed to be entirely different,

appearing to be dependent upon the low surface energy imparted to the fiber surface by a monomolecular layer of oriented fluorinated hydrocarbon chains.

9. Surfaces and soiling tendencies of certain other fibers were compared briefly with those of cotton. Nylon, Dacron, and viscose rayon fibers all have smoother surfaces than cotton, but this feature evidently does not necessarily impart higher soil resistance.

10. It would appear from these investigations that a theoretical study of surface energy effects in relation to soiling of fibers might contribute significantly to a solution of the problem of soil resistance.

Acknowledgments

We are indebted to the Dan River Mills for scouring, bleaching, and mercerization of the test fabric. Laboratory samples of the commercial soil retardants were donated by the respective manufacturers. Samples of chemically modified fabrics were obtained from the Cotton Chemical Processing Section of the SURDD. The Radioactive Tracer Laboratory was used through the courtesy of the Analytical Section, SURDD.

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Mechanism of Rupture of Jute Yarn Under Tensile Stress

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Introduction

The primary characteristics of a jute yarn which determine its serviceability and wear in the course of manufacture and use are irregularity and tensile strength. In a previous paper [1], the various causes of irregularity of jute yarn and suitable methods of analyzing them have been indicated. Among the important fiber properties contributing towards yarn irregularity, particular reference was made to fineness and length. The present paper deals with tensile strength; the effects of length, number, and tensile strength of the fibers have been considered, along with the yarn geometry as described by grist, diameter, twist, and specimen length. In this connection, the analytical expressions derived by Daniel [3], Foster et al. [5], Mark [7], and Platt [9] have been freely used.

The material consists of nine samples of average quality burlap warp, burlap weft, and sacking warp yarns, three of each variety. The quality characteristics of the yarn as measured by routine methods are indicated in Table I.

Measurement of Fiber Properties

Length — L

Each sample of yarn is cut into 24-in. lengths and untwisted; the fibers are carefully removed, and those from the two ends are rejected. The fibers are thoroughly mixed and formed into a lump from which tufts are drawn at random to make a smaller sample. The length of fibers in the sub-sample is measured; approximately 2000 individual measurements are carried out in order to obtain average fiber length and length distribution.

Number of Fibers/Cross Section of Yarn — N

Samples are prepared as indicated above. Fibers are drawn from each sample, cut into 2-in. lengths, and weighed. About 150 fibers are measured; the average weight/unit length is then obtained. Since the ratio of the weight/unit length of yarn to the weight/unit length of fibers gives an estimate of fiber number (neglecting the effect of twist), the following relation is used:

$$N = \frac{\text{Wt./unit length of yarn}}{\text{Wt./unit length of fiber}} = \frac{G \times 453.6}{14{,}400 \times 36 \times w} = 8.75 \times 10^{-4} \times \frac{G}{w}$$

where G = yarn grist in lbs./spindle of 14,400 yd. and w = wt./in. of fiber (g.).

Tensile Strength of Fibers — s_z

The fibers separated from the yarns are cut into pieces of given length and their individual weights taken. The breaking strength of the fibers at specimen length 0.5, 2.0, 4.0, 6.0, and 12.0 cm. between grips is determined, using a recording extensometer. Approximately 50 tests are performed for each specimen length.

TABLE I. Quality Characteristics of the Yarns under Test

	Burlap warp				Burlap weft				Sacking warp			
	1	2	3	Mean	1	2	3	Mean	1	2	3	Mean
Grist (lb.)	8.24	8.83	9.10	8.72	11.01	9.40	11.54	10.65	9.70	9.71	10.11	9.84
T.P.I.	4.38	4.07	4.25	4.23	4.00	3.70	3.62	3.77	4.30	4.22	4.23	4.25
Wt. C.V.%	30.0	31.5	30.7	30.7	32.1	33.4	32.3	32.6	32.7	32.0	37.2	34.0
α(lb./grist)	0.07	0.13	0.12	0.11	0.09	0.11	0.12	0.11	0.17	0.17	0.22	0.19

Measurement of Yarn Properties

Grist — G

This is determined from the mean weight of five 75-yd. hanks.

Twist/Inch

The number of turns per 5-in. length of the yarn is measured on a Goodbrand Twist Tester. The twist/in. is then calculated from the mean of 20 tests from each sample.

Yarn Diameter — D

This is measured by using a projection microscope.

Tensile Strength of Yarn — S_x

This is determined on a Goodbrand Single Thread Tester using specimen lengths of 2, 4, 8, 16, and 32 in. The rate of traverse of the driving head of the machine used is 12 in./min. For each length, 100 tests are carried out.

Theoretical Derivations and Results

Figure 1 shows the average frequency and cumulative frequency distribution curves for fiber lengths in the three types of yarns. It will be seen that the numerical proportions of fibers shorter than 1 cm. is less than 2%, and the maximum fiber length is 25 cm. The mean fiber length is about 9 cm. in both burlap warp and burlap weft, and 10 cm. in the sacking warp.

In the analytical treatment to follow, the yarns are assumed to be uniform, having the same frequency distribution of fiber length for cross sections at all parts. Accordingly, at specimen length 25 cm. or more, a yarn will be composed wholly of discontinuous fibers held in position by mutual entanglement and frictional force. As the specimen length is reduced, there will be more and more continuous fibers held between both grips. Since the proportions of continuous and discontinuous fibers as well as other factors will contribute towards the tensile strength of a yarn with specimen length less than 25 cm., the problem rests upon (*a*) estimation of the number of continuous and discontinuous fibers, (*b*) evaluation of average strength per fiber in a continuous bundle held between both grips, (*c*) consideration of effect of twist in a bundle of continuous fibers, and (*d*) calculation of frictional force due to discontinuous fibers. The requirements under (*a*) and (*b*) would not arise for a specimen length equal to or greater than 25 cm., since there are only discontinuous fibers to consider. In this case, the effects of twist and frictional force may be regarded as randomly distributed, leading to regions of imperfections. The number of imperfections may be estimated using Epstein's theory of extreme values [4], according to which the system may be conceived as a long chain of links of different strength joined in series. In a separate communication [2] the theory has been applied to estimate the imperfection density in ramie and jute fibers.

Estimation of the Number of Continuous and Discontinuous Fibers

Using the expressions derived by Foster, Gregory, and Womersley [5] for the number of fibers crossing

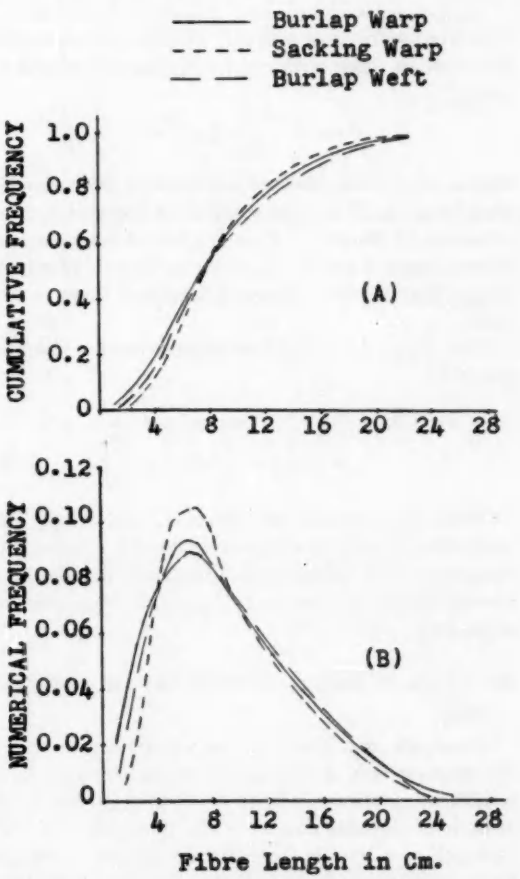

Fig. 1. Frequency distribution of fiber length in the three types of yarn. (*A*) cumulative frequency, (*B*) numerical frequency.

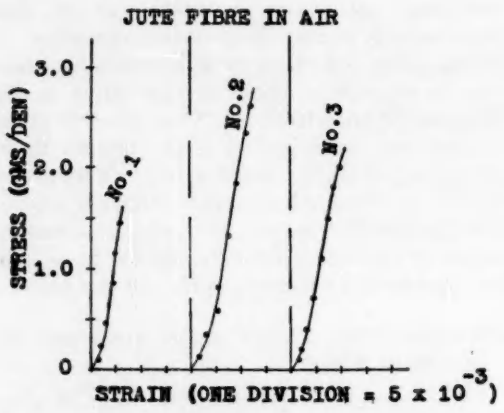

Fig. 2. Stress–strain curves.

two cross sections of a sliver, which is substantially the same as those obtained by Köhler [6] for cotton yarn

$$N_{c(x)} = \frac{NF_x}{L}(L_x - x)$$

where $N_{c(x)}$ = number of continuous fibers/specimen length x, N = total number of fibers that cross a section of the yarn, F_x = fractional frequency of fibers longer than x, L_x = mean length of fibers longer than x, and L = mean length of fibers in the yarn.

Therefore, the number of discontinuous fibers is given by

$$N_{d(x)} = N - N_{c(x)} = N\left[1 - \frac{F_x}{L}(L_x - x)\right] \qquad (1.0)$$

Thus, from measurements of L and N by the method indicated in the previous section, using the frequency and cumulative frequency distribution curves shown in Figure 1, $N_{c(x)}$ and $N_{d(x)}$ can be estimated.

Evaluation of Average Strength/Fiber in a Bundle $- T_x$

Inasmuch as a fiber may be regarded as a chain the weakest link of which determines its strength, a bundle of continuous fiber may be regarded as a system of parallel chains. The derivation of the strength of a bundle from measurements on single fibers is given by Daniel [3]; the conditions implied in the method are that (1) the load elongation curves for the fibers in the bundle are similar in form, (2) the load elongation curves are linear up to the breaking point, (3) the distribution of Young's modulus (i.e., breaking load/breaking extension) and extensibility percent are independent of each other, (4) the standardized variance (i.e., square of the coefficient of variation) of Young's modulus is smaller than that of extensibility percent, and (5) the number of fibers in the bundle is large.

It will be seen from Figures 2 and 3 that conditions (1), (2), and (3) are fulfilled. The standardized variance of Young's modulus is about half that of extensibility percent, indicating that (4) also holds good for jute. The hypothesis involved in (5) may be supposed to apply, at least approximately, to jute yarns.

If $\theta(\sigma)$ is the probability density of the breaking load σ for a fiber, the chance of the fiber breaking under the load s may be represented by

$$\int_0^s \theta(\sigma)d\sigma = b(s) = a\left(\frac{1}{s}\right) = a(W) \qquad (1.1)$$

where W may be called the "weakness" of the fiber.

The total load P supported by a yarn containing a large number of fibers per cross section N is

$$P = sN\int_s^\infty \theta(\sigma)d\sigma = \frac{N[1 - a(W)]}{W} \qquad (1.2)$$

where s or $\frac{1}{W}$ is the applied load supported by each of the surviving fibers in the yarn.

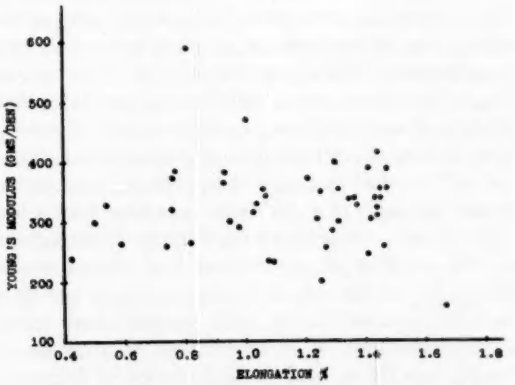

Fig. 3. Distribution of Young's modulus and percent elongation of fibers.

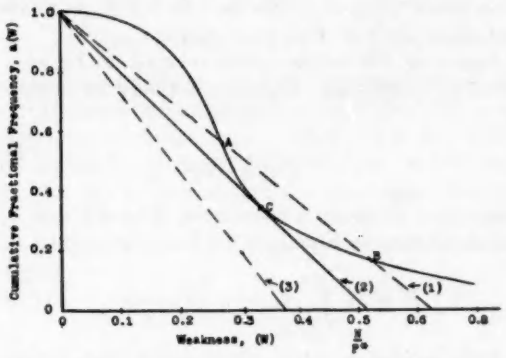

Fig. 4. Typical cumulative frequency distribution curves for fiber weakness.

The breaking load P' occurs when $W = W'$ satisfies the condition

$$\frac{d}{dW'}\left[\frac{1 - a(W')}{W'}\right] = 0 \qquad (1.3)$$

From (1.1) it will be seen that the function $a(W)$ decreases continuously from 1 to 0 as W increases from 0 to infinity.

A graphical method of determining W' and P' is as follows: the relation between $a(W)$ and W as obtained from experimental results may be typified by a curve given in Figure 4. For a given load P on the yarn, the average load per fiber is $\frac{P}{N}$; the corresponding value of W is $\frac{N}{P}$. If a straight line is drawn through the points (1, 0) and $\left(0, \frac{N}{P}\right)$ in Figure 4, evidently three different cases may arise; the straight line (1) intersects the curve at two points A and B, (2) touches the cuve at C, or (3) does not meet the curve at all.

In case (1) the yarn will remain under equlibrium when the applied load for values of W corresponds to those for points on the curve lying between A and B. Case (2) gives the condition for the breaking load. The equilibrium is just possible at the value of W given by the point C. If the load is increased slightly more, the yarn will rupture at once. Hence the W value of C is W' and that of the point where the line meets the abscissa is $\frac{N}{P'}$. Therefore, to determine $\frac{P'}{N}$ (the average strength of a fiber in a bundle), the simple method may be to draw a straight line from the point (1, 0) just touching the experimentally determined $a(W)$ vs. W curve. The reciprocal of the W value for the point where this line meets the abscissa gives the required result. Case (3) occurs when the applied load exceeds the breaking load for the yarn and is therefore of no interest for the purpose in view.

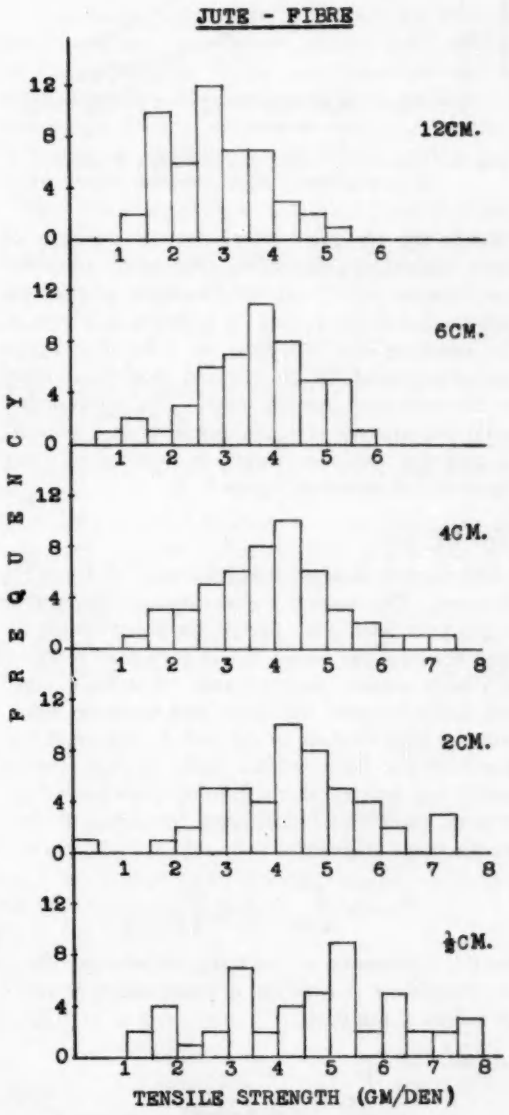

Fig. 5. Histograms of fiber strength for different specimen lengths.

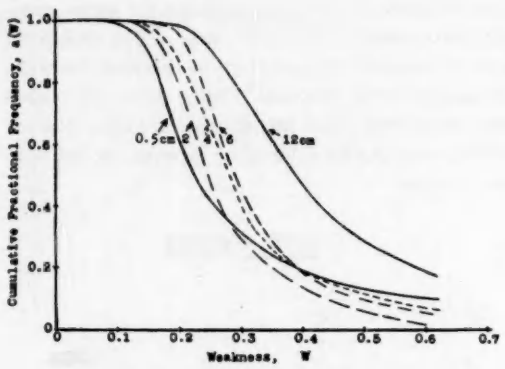

Fig. 6. Cumulative frequency distribution of weakness; fibers of different specimen lengths.

From the observed histograms of strength of fibers constituting the yarns (Figure 5), the relation between $a(W)$ and W has been plotted for each specimen length used; it is shown in Figure 6. The breaking load per fiber in a bundle, T_z, is then determined by the method described above for the specimen lengths used. The relation between the average strength per fiber in a bundle, T_z, and the specimen length is determined from Figure 6 and shown in Figure 7.

Effect of Twist

The method suggested in the work of Platt [9] was used. The fibers in a yarn do not all lie parallel to the yarn axis, and, except for a few which lie along the axis, the center line of each fiber remains on a helix around the yarn axis. The helix angle (the angle between the fibers and the yarn axis), increases with increase in the radial distance of the fiber from the center of the yarn. Under certain simplifying assumptions regarding yarn geometry, the total axial load P supported by a yarn of continuous fibers is given by

$$P = 2\pi \int_{r=0}^{R} f_r \frac{rdr}{(1 + 4\pi^2\tau^2r^2)} \qquad (1.4)$$

where f_r = stress on a fiber lying at distance r from the yarn axis, τ = twist/in. of yarn, and R = average radius of the yarn.

Further,

$$e_r = \frac{e_0}{1 + 4\pi^2\tau^2r^2} \qquad (1.5)$$

where e_r and e_0 are the strains produced by the load P on fibers lying at a distance r from the yarn axis and along the yarn axis respectively.

Assuming the stress–strain relation to be governed by Hook's law, Equation 1.5 may be written as

$$f_r = \frac{f_0}{1 + 4\pi^2\tau^2r^2} \qquad (1.6)$$

where f_0 = stress on a fiber along the yarn axis.

Substituting in Equation 1.4 from Equation 1.6,

$$P = 2\pi \int_{r=0}^{R} f_0 \frac{rdr}{(1 + 4\pi^2\tau^2r^2)^2} \qquad (1.7)$$

After expanding into a power series, integrating, and neglecting terms containing powers of R greater than 4, which is justifiable since $4\pi^2\tau^2R^2 < 1$, Equation 1.7 reduces to

$$P = P_0(1 - 4\pi^2R^2\tau^2)$$

where

$$P_0 = \pi R^2 f_0.$$

Thus, if P represents the breaking load with twist τ, P_0 will be its strength when the twist is 0; i.e., the fibers are straight and parallel with the yarn axis. The effect of twist, therefore, is to reduce the theoretical strength of the yarn by a factor T_f given by

$$T_f = (1 - 4\pi^2\tau^2R^2) \qquad (1.8)$$

τ and R are the values at the instant of rupture of the yarn; both these quantities will diminish continuously as the elongation increases. From the general principle of elasticity of isotropic solids, the lateral compression due to an axial load depends upon the modulus of torsional rigidity n and

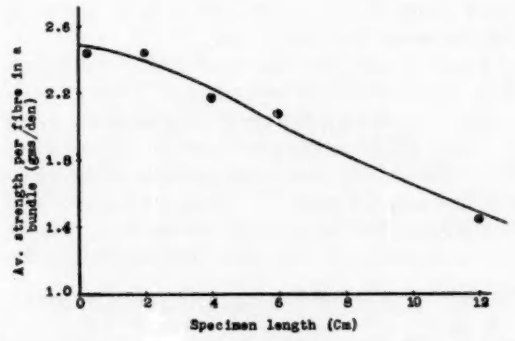

Fig. 7. Relation between average strength per fiber in a bundle and the specimen length.

Young's modulus of bending or tension E. Depending upon whether or not $\frac{1}{n} - \frac{2}{E}$ is positive or negative, the fibers will be compressed or opened out by the action of the axial load in the yarn. An approximate calculation using $n = 1.1 \times 10^{10}$ dynes/cm.^{2} and $E = 9 \times 10^{10}$ dynes/cm.^{2} for jute [8, 12, 13] shows that the compressive force is positive. If τ_s and R_s are the corresponding values at no load, the following approximate relations will hold [9]

$$\tau = \frac{\tau_s}{1 + e_r} \tag{1.9}$$

$$R^2 = \frac{R_s^2}{1 + e_r} \tag{2.0}$$

where e_r is the strain produced in the yarn at rupture.

Substituting (1.9) and (2.0) in (1.8),

$$T_f = 1 - \frac{4\pi^2\tau_s^2R_s^2}{(1 + e_r)^3}$$

$$= 1 - 4\pi^2\tau_s^2R_s^2(1 - 3e_r) \tag{2.1}$$

since e_r is small, of the order of 0.05, for jute yarns.

Cohesive Force Due to Discontinuous Fibers — Q_x

As has already been indicated, the fibers passing through a cross section are discontinuous when the specimen length is 25 cm. or more. The strength of the yarn is then wholly due to frictional force between the fibers, which decreases in accordance with the theory of imperfections as the length is increased. Assuming Q_0, the maximum frictional force between fibers, to be represented by the strength of the yarn at length 25 cm. and that the force is proportional to the number of discontinuous fibers,

$$Q_x = Q_0 \frac{Nd(x)}{N}$$

where Q_x = frictional force at specimen length $x < 25$ cm.

$\therefore$ from (1.0),

$$Q_x = Q_0\left[1 - \frac{F_x}{L}(L_x - x)\right] \tag{2.2}$$

Calculations

From the analytical treatment as given above, the strength of a jute yarn of specimen length less than 25 cm. is given by the following equation:

$$S_x = N_{c(x)} \cdot T_x \cdot T_f + Q_x$$

$$= \frac{NF_x}{L}(L_x - x) \cdot T_x \cdot T_f + Q_0\left[(1 - \frac{F_x}{L}(L_x - x)\right]$$

$$= \frac{F_x}{L}(L_x - x)[N \cdot T_x \cdot T_f - Q_0] + Q_0 \tag{2.3}$$

Thus it is possible to calculate the yarn strength from measurements of length, number, and strength of the component fibers, and measurements of twist, diameter, and strength of the yarn at specimen length 25 cm. In order to eliminate variation in the weight of different samples, the strength Q_0 is expressed in lb./grist.

Strength of samples of specimen lengths greater than 25 cm., S_l, can be calculated by applying the following expressions (Mark [7]) as deduced from probability considerations

$$S_l = S_0 - \alpha \log e \frac{l}{l_0} \tag{2.4}$$

where S_0 = strength of 25 cm. length, α = imperfection coefficient, and l_0 = 25 cm.

By a suitable choice of value for α, the calculated strength can be made to agree with the observed data.

As an example, the method of obtaining the parameters required for calculation of strength of a burlap warp yarn with the specimen length 10 cm. is indicated below.

The average number of fibers/cross section = 146.4

The number/grist = $\frac{146.4}{8.7}$ = 16.8

(8.7 lbs. = the average grist of the yarn)

F_x = 0.32 (see Figure 1)

L_x = 14.22 cm. (calculated from Figure 1)

T_x = 1.65 g./den. (see Figure 7)

= 1.65 × 19 g. (average denier of component fibers is 19)

= $\frac{1.65 \times 19}{453.6}$ lb.

= 0.069 lb.

$T_f = 1 - 4\pi^2\tau_s^2R_s^2(1 - 3e_r)$

Average twist/in., τ_s ≈ 4.0

Radius of yarn, R_s = 0.017 in.

Elongation/unit length of yarn as measured, e_r = 0.05

$\therefore$ T_f = 0.84

Average strength of the yarn of 25 cm. specimen length = 7.31 lb.

$\therefore$ Q_0 in lb./grist $= \frac{7.31}{8.7}$ = 0.84

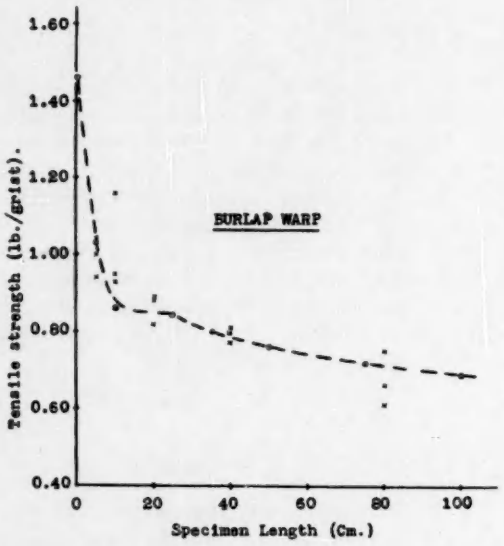

Fig. 8a. Variation of tensile strength with specimen length for burlap warp. o = calculated values; x = observed values.

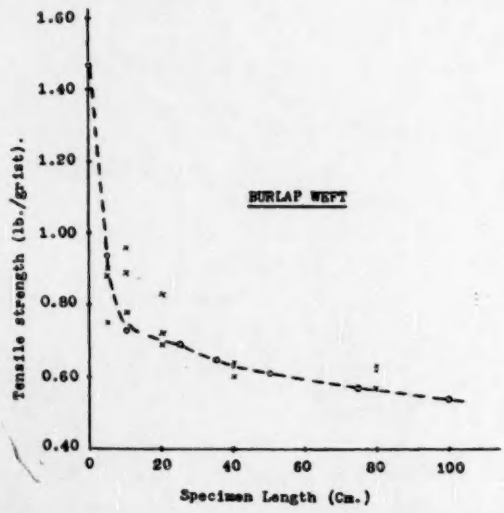

Fig. 8b. Variation of tensile strength with specimen length for burlap weft. o = calculated values; x = observed values.

Substituting in Equation 2.3, the yarn strength with 10 cm. specimen length is calculated to be 0.86 lb./grist.

The average α-value required for calculation of strength with specimen length greater than 25 cm. has been found to be 0.11 for burlap warp yarn.

Figure 8 shows the calculated curves as well as the observed results for the burlap warp, burlap weft, and sacking warp yarns when the specimen length is varied from 5 to 100 cm.

It has been observed that the number of fibers per cross section per unit grist, N, and the values of F_x, L_x, T_x, and T_f for burlap weft and sacking warp are not significantly different from those for burlap warp. The average values of L and Q_0 for the three different types of yarn are as shown in Table II.

Discussion

The discontinuous nature of the strength–length curve as indicated in the present work was noted previously by Sommer [15] and Sen and Nodder [14]. Recently, Platt [10] has indicated a similar trend in the curve for staple viscose yarns. It is interesting to note that the shape of the distribution curve for continuous fibers in staple yarn, as given by Platt [10], is very similar to that observed for the jute yarns (Figure 9).

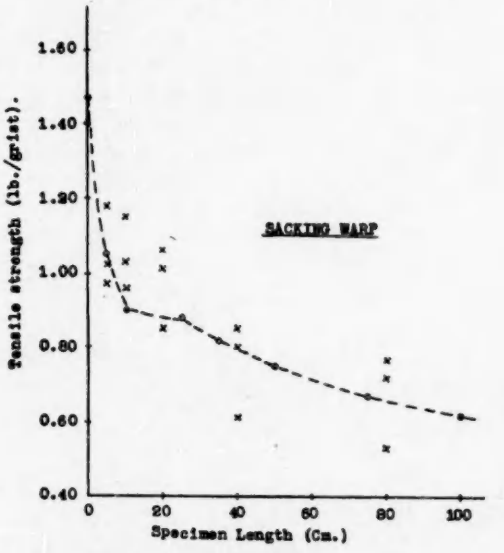

Fig. 8c. Variation of tensile strength with specimen length for sacking warp. o = calculated values; x = observed values.

From Figure 8 it can be seen that the agreement between the calculated and the observed points is fairly close for the burlap warp and burlap weft yarns. For the sacking warp, the observed points are rather widely scattered about the theoretical curve; this is probably due to the average irregularity of the samples being high in comparison with the burlap yarns (Table I).

The present work demonstrates clearly that the main factors governing the strength of yarns are (*a*) strength, length, length distribution, and fineness of the constituent fibers, (*b*) frictional forces between the fibers, and (*c*) the imperfection coefficient α of the yarn. Of these, the fiber characters under (*a*) are predominant when the gauge length is less than 10 in.; at a length of about 10 in., when the fibers in the yarn are all discontinuous, the strength is chiefly due to the frictional forces between the fibers. The strength at lengths greater than 10 in. is determined to a large extent by the imperfection coefficient α. Since the imperfection arises from nonuniform distribution of fibers, the coefficient should be strongly correlated with Wt.C.V.%. This is shown in Figure 10.

At this stage it may be pointed out that in the current practice of evaluating yarn quality, both quality ratio and Wt.C.V.% are determined. Because the strength at lengths greater than 10 in. is influenced by α or Wt.C.V.%, the quality ratio on the basis of strength at 24 in., as used in India, is not an independent measure. In order to avoid the effect of weight variation, a more suitable procedure therefore should be to test for strength at a gauge length of 10 in.

The condition of independence of Young's modulus and breaking extension, as postulated in this work, will certainly hold when the stress–strain curve of a fiber is linear, at least, in the region of $\pm 3 \times$ standard deviation about the mean elongation at break. Inasmuch as most of the cellulose fibers such as cotton, flax, sisal, etc. show a linear stress–strain relationship over a considerable region near the breaking point, it is believed that the method of analysis described would apply equally to yarns of cellulose fibers other than jute. Consideration of the effect of interaction between the variability of fiber strength and twist was omitted in the analysis with a view to simplification of the treatment. However, from the derivations of Platt, Klein, and Hamburger [11], it can be shown that the effect is negligible for jute yarns having a surface helix angle of 20–25°, $e_m = 2\%$, $v = 20$, and $a/b \approx 0$ (compare with Sansevieria fiber).

TABLE II. Average Values of L and Q_0

	L (cm.)	Q_0 (lb./grist)
Burlap warp	8.92	0.84
Burlap weft	9.17	0.70
Sacking warp	10.11	0.86

Acknowledgment

The authors wish to thank Dr. W. G. Macmillan, Research Director, Indian Jute Mills Association Research Institute, for permission to publish this work.

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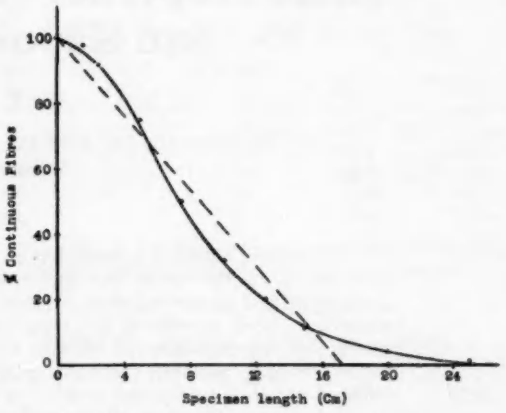

Fig. 9. Distribution of continuous fibers with specimen length in jute yarns.

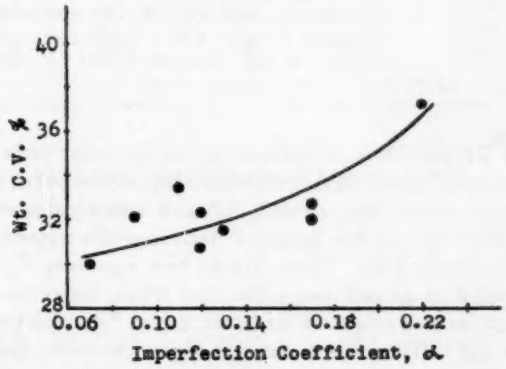

Fig. 10. Relation between the imperfection coefficient and weight C.V.% for the yarns.

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Some Properties of Native Hemp, Jute, and Kapok Celluloses[1]

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Abstract

The general chemical composition of untreated fibers of hemp, jute, and kapok has been studied, and the results have been compared to the composition of the corresponding α-celluloses and of the cellulose nitrates obtained by direct nitration of the original materials. After correction for nonglucose sugar residues, the data indicated the presence of approximately 80, 60, and 40% cellulose, respectively, in the native fibers. Unlike the hemp and jute, the kapok cellulose could not be nitrated to completion. No evidence was obtained for any association between α-cellulose and xylan in the jute.

The average degree of polymerization of the nitrates was 4800 for the hemp, 4700 for the jute, and 3300 for the kapok cellulose, the first two values being the same as those found previously for native cotton and flax celluloses. The molecular weight distributions contained only one maximum and were symmetrical for hemp and jute. For kapok a curve with a slight right hand skewness was obtained. The results were compared to data obtained earlier for other bast and seed fibers.

PREVIOUS investigations on the molecular properties of various native celluloses included celluloses from cotton, flax, ramie [21], and milkweed floss [25], and from ten species of deciduous and coniferous woods [22]. These studies have now been extended to include two other bast fibers, hemp and jute, as well as a third seed hair, kapok. In addition to the cellulose constituent of these materials, the general chemical composition of the native fibers has also been investigated.

True hemp (*Cannabis sativa*) is a bast fiber which is now used mostly for cordage. It is grown in several European countries; Italy is reported to produce the best quality. Earlier studies of this product seem to have been limited to its chemical composition. It is stated to contain 70–80% α-cellulose, 2–5% lignin, and 15–20% hemicelluloses [6, 7]. Jute (various species of *Corchorus*) is, together with cotton, more

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widely used for textile purposes than any other vegetable fiber. It is extensively grown in East Pakistan and India, and is used chiefly for making sacks, upholstery, and rugs. Unlike that of hemp, the chemistry of the jute fiber has been at least partly elucidated. According to Sarkar and co-workers [6, 16, 18], jute contains approximately 60% α-cellulose, 10–15% lignin, and 25–30% hemicelluloses. The larger portion of the latter consists of a 1,4-linked xylan polysaccharide containing 3-*O*-methyl-D-glucuronic acid side-chains linked through the 3-position [5, 17]. α-celluloses isolated from jute by a variety of different methods had degrees of polymerization within the range of 400 to 1200 [6].

Kapok (*Ceiba pentandra*) is a seed fiber cultivated in the East Indies, commonly used for upholstery and lifebelts. Unlike other seed hairs such as cotton or milkweed floss, the kapok fiber consists of several cells and has a very wide lumen and thin cell wall. According to Zapf [27] it contains 35% cellulose, 45% hemicelluloses, and 18% lignin. The same author has also studied the molecular properties of the cellulose component. The latter was isolated by delignification with chlorine dioxide and alkaline extraction. In spite of these rather severe treatments, the resulting "cellulose" still contained 15% hemicelluloses. Viscosity measurements on the nitrate derivative indicated an average molecular weight of 1500. Fractional precipitation resulted in a chain-length distribution which contained three maxima and which extended from a D.P. of 70 to 2200.

Results

Untreated fibers of Italian hemp, Indian jute, and kapok were extracted with ethanol-benzene and cold water. Some data for the chemical composition of the products, all of which were obtained by standard procedures, are presented in Table I. The hemp fibers apparently contained almost twice as much cellulose as the kapok, and had a much lower content of pentosan and lignin. The large number of acetyl groups in the kapok is notable, as is its high content of uronic anhydride. Jute occupies an intermediate position between the other two fibers as far as chemical composition is concerned, the values found being in close agreement with those given by Sarkar, Mazumdar, and Pal [17].

Earlier investigations [21, 22] indicated that direct nitration of native cellulosic materials constitutes a means for quantitative isolation of a usually undegraded cellulose. Extractive-free fibers of hemp, jute, and kapok were accordingly nitrated for various lengths of time with a non-degrading acid mixture and isolated as described previously [21, 22]. Intrinsic viscosities of the nitrates were determined in acetone or ethyl acetate, corrected for ni-

TABLE I. Analytical Data for Untreated Hemp, Jute, and Kapok Fibers

(All values in percent of extractive-free material)

Component	Hemp	Jute	Kapok
Alpha-cellulose	78.3	59.4	43.2
Pentosan	4.15	15.1	24.4
Lignin	2.90	12.9	15.1
Ash	0.53	0.62	0.76
Acetyl	1.32	3.82	8.0
Uronic anhydride	2.50	4.47	6.61

TABLE II. Nitration of Hemp Fibers at +17° C.

Time, hr.	Yield,* %	Nitrogen, %	$[\eta]$**	D.P.
1	82.8	13.82	37.5	4780
2	81.3	13.78	36.4	4580
3	81.8	13.80	36.8	4700
5	80.2	13.80	35.2	4200
7	79.7	13.87	31.0	3030

* Cellulose in percent of extractive-free oven-dry material.
** Dl/g. in acetone, uncorrected for nitrate substitution.

TABLE III. Nitration of Jute Fibers at +17° C.

Time, hr.	Yield,* %	Nitrogen, %	$[\eta]$**	D.P.
1	60.8	13.73	28.0	2750
2	61.0	13.75	36.5	4720
3	61.2	13.80	36.7	4620
5	61.1	13.81	36.7	4580
7	60.9	13.80	36.8	4650

* Cellulose in percent of extractive-free oven-dry material.
** Dl/g. in acetone, uncorrected for nitrate substitution.

TABLE IV. Nitration of Kapok Fibers at +17° C.

Time, hr.	Yield,* %	Nitrogen, %	$[\eta]$**	D.P.
1	14.7	13.71	27.9	2760
2	28.2	13.85	32.1	3270
3	27.7	13.85	32.5	3360
5	28.3	13.80	30.1	3000
7	25.3	13.70	27.8	2780

* Cellulose in percent of extractive-free oven-dry material.
** Dl/g. in acetone, uncorrected for nitrate substitution.

trate substitution and effects of rate of shear, and converted to degrees of polymerization as described elsewhere [21, 22]. The results obtained are presented in Tables II–IV. The hemp cellulose was isolated in an approximate yield of 82%, calculated as cellulose in the original material, and was stable under the nitration conditions for the first 3 hr. The jute was nitrated at the same rate, but was more stable, no degradation being noticeable within the first 7 hr. The yield remained constant throughout at 61%. The kapok gave a nitrate in a yield of only 28% and was stable for only 3 hr. in the nitration mixture.

Direct nitration of cellulosic materials has previously been found to give a nitrate derivative in a yield corresponding closely to the known content of true cellulose in the product [22]. In order to establish whether or not this applied in the present case, chlorine holocelluloses were prepared from the extractive-free fibers and exhaustively extracted with alkali. The carbohydrate composition of the α-celluloses thus obtained was determined by quantitative paper chromatography after hydrolysis. The glucan portion of the α-cellulose was assumed to represent the cellulose present in the native fiber. In the same way, the corresponding nitrates were denitrated, hydrolyzed, and analyzed for constituent sugars. For comparative purposes, the native fibers were also subjected to the same analytical procedure. The results are summarized in Table V, which presents the relative amounts of neutral anhydrosugars present in the three preparations from each of the three fibers. These values are given in percent of the original extractive-free material, and were calculated assuming the latter to be composed of lignin, ash, acetyl, uronic anhydride, and residues of neutral sugars.

The hemp fiber apparently contained, besides uronic acid units, galactose, glucose, mannose, arabinose, and xylose residues. Minor amounts of rhamnose might also have been present [7]. More than 80% of the material was composed of a glucan, with mannan constituting the main part of the remainder. The α-cellulose contained no anhydrogalactose units, but small amounts of mannose, arabinose, and xylose residues were still present. The nitrate contained only a minor quantity of mannan besides the main glucan component, thus indicating the ability of the nitration procedure to eliminate minor amounts of nonglucose sugar residues, with the exception of mannose.

The jute fiber contained less glucan and more xylan than the hemp. The α-cellulose and the nitrate were composed almost exclusively of glucan, with only a small portion of xylan present in the former and a trace of mannan in the latter. In addition to the sugar residues found here, the presence of rhamnose has also been reported [2, 3, 11]. The native kapok fiber had a high content of xylan, although not as high as that found for milkweed floss, 35% [25]. With the exception of the galactose, the nonglucose sugar residues in the original product were still present in small amounts in the α-cellulose and the nitrate.

As can be seen from Tables II–IV, the maximum degree of polymerization of the three celluloses was for hemp 4800, for jute 4700, and for kapok 3300. The possibility that some rapid initial depolymerization occurred during the nitration cannot, of course, be entirely excluded, but appears improbable.

For an approximate estimation of the chain-length distribution of the three nitrates, a portion of each was dissolved in aqueous acetone and fractionally precipitated in duplicate experiments by slowly removing the solvent. Twenty to thirty fractions of approximately the same size were isolated, weighed, and analyzed for their nitrogen content and intrinsic viscosity. The integral curves were constructed in

TABLE V. Carbohydrate Composition of Various Hemp, Jute, and Kapok Products

(All values in percent of extractive-free native material)

	Hemp			Jute			Kapok		
Component	Native material	α-cellulose	Nitrate	Native material	α-cellulose	Nitrate	Native material	α-cellulose	Nitrate
Galactan	1.5	Nil	Nil	Trace	Nil	Nil	1.2	Nil	Nil
Glucan	83.3	76.5	80.3	65.6	58.2	60.6	47.4	40.2	27.7
Mannan	5.7	0.9	1.7	2.7	Nil	0.4	Trace	0.5	0.3
Araban	1.0	0.4	Nil	0.4	Nil	Nil	Trace	0.2	0.1
Xylan	1.3	0.5	Nil	9.5	1.2	Nil	20.9	2.3	0.2

the usual way and from these the differential, or weight frequency, distribution curves presented in Figures 1–3 were obtained by graphical differentiation. Some depolymerization evidently occurred during the fractionation; the D.P. limits given are therefore of little significance. The hemp and the jute celluloses had a symmetrical frequency distribution, containing only one maximum. The latter was the case also with the kapok cellulose, the weight distribution of which, however, exhibited a slight right hand skewness. The lower D.P. limit in all three celluloses was within the range of 1000 to 1500.

Discussion

If the amount of glucan in the native hemp (Table V) is compared to that found in its α-cellulose and nitrate derivative, it is seen that some of the glucose residues in the native fiber probably originated from a polysaccharide other than cellulose. The same difference between the quantities of glucan and of cellulose is noticed for the jute and kapok fibers. Similar results were obtained earlier with a series of woods; it was suggested that the presence of a glucomannan polysaccharide might at least partially explain this phenomenon [23].

The nitration, when applied to the hemp and jute, indicated a somewhat higher content of cellulose in these fibers than was found by the α-cellulose method. The nitrates consisted of almost pure cellulose; it is possible that the difference was due to losses of carbohydrates during the isolation of the α-celluloses. It was clear that in both cases the nitrated products represented virtually the entire quantity of cellulose present. The cellulose content of the hemp, approximately 80%, was somewhat higher than that reported elsewhere for this fiber [6], whereas the value of 60% for the jute checked excellently with data presented by other workers [6, 12].

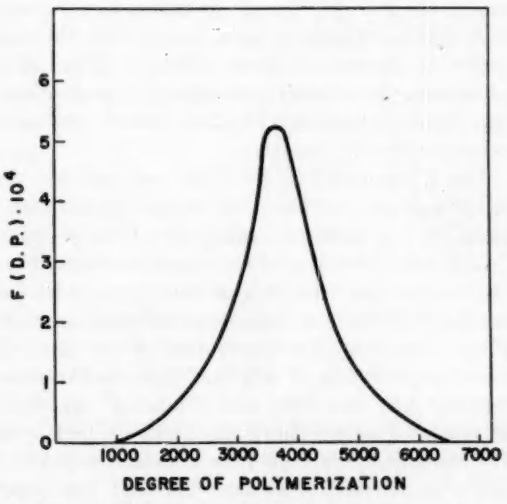

Fig. 1. Weight frequency distribution curve for hemp cellulose.

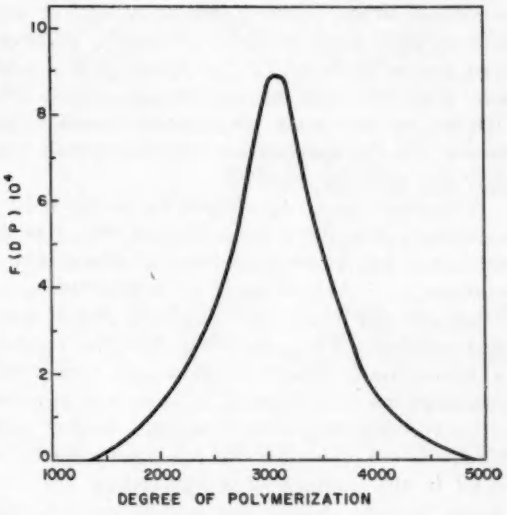

Fig. 2. Weight frequency distribution curve for jute cellulose.

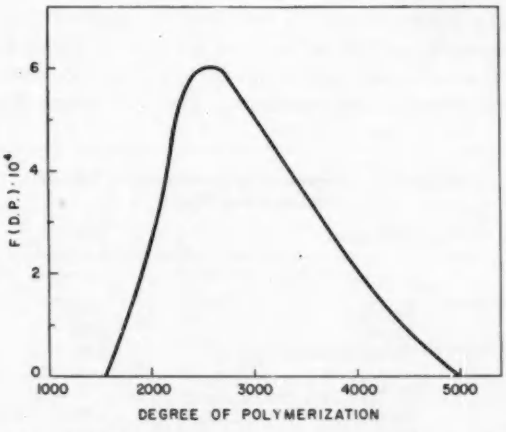

Fig. 3. Weight frequency distribution curve for kapok cellulose.

In the case of the kapok, direct nitration of the untreated fiber did not result in isolation of a cellulose nitrate in a yield comparable to the content of α-cellulose, the amount of the former being only 69% of the latter. As was mentioned above, Zapf [27] found native kapok to contain 35% cellulose, but if a correction is applied for the hemicellulose content of his crude cellulose, a figure of 29% is obtained. This is only slightly higher than the yield noticed here on nitration, 27.7%. On the other hand, the glucan content of both the original material and the α-cellulose would definitely indicate a cellulose content of approximately 40%. Similarly, milkweed floss was earlier found [25] to contain 40% α-cellulose, while the yield on nitration was only 27.9%. The reason for these discrepancies remains unknown; the phenomenon was not encountered with any other cellulosic material.

It has been repeatedly claimed by Sarkar and his co-workers [13, 19] that α-celluloses from jute do not contain any xylose or arabinose residues. Other workers [1, 4, 11], however, have been unable to isolate any jute α-celluloses completely free of these sugar residues. The present data show that removal of the final traces of anhydroxylose units from a jute α-cellulose is very difficult. The absence of pentoses in the corresponding nitrate suggests, on the other hand, that the reason for this is probably not to be found in the presence of a hypothetical chemical linkage between glucose and pentose residues, but rather in adsorption effects.

In the present study, use was made of the relationship between the intrinsic viscosity as measured at a shear rate of 500 sec^{-1} and the weight-average molecular weight of cellulose nitrates developed by Newman, Loeb, and Conrad [15] from sedimentation-diffusion measurements. The D.P. values thus obtained are somewhat lower than those reported by Schulz and Marx [20], who used a calibration curve developed by Meyerhoff [14] on the basis of ultracentrifuge data. Recently, Holtzer, Benoit, and Doty [9] and, in a somewhat later investigation, Hunt, Newman, Scheraga, and Flory [10] have developed relationships between the intrinsic viscosity of cellulose nitrates and their weight-average molecular weight as determined from light scattering measurements. Their results agree excellently, and indicate much higher degrees of polymerization than those obtained earlier. The nitrates studied by these workers were, however, of a much lower average molecular weight than those employed by either Newman, Loeb, and Conrad or Meyerhoff.

TABLE VI. Degree of Polymerization of Various Seed and Bast Fibers

Material	D.P.
Seed hairs	
Cotton	4700
Kapok	3300
Milkweed floss	5700
Bast fibers	
Flax	4700
Hemp	4800
Jute	4700
Ramie	5800

In Table VI a summary is presented of the D.P. data so far obtained in the present series of investigations for seed and bast fibers. Among the seed hairs, milkweed floss had, rather surprisingly, the highest D.P. Cotton was somewhat lower in molecular weight, although it should be mentioned that the comparison might not be entirely strict, the milkweed floss having been collected from unopened pods and the cotton from opened bolls [*cf.* 8]. The kapok cellulose had a much lower molecular weight, which was, however, considerably higher than that reported by Zapf [27].

Among the bast fibers, flax, hemp, and jute have almost the same degree of polymerization, whereas that of ramie is higher. With the exception of the kapok, the total D.P. range is rather narrow, only 5000–6000. This range is the same as that observed earlier for a series of wood celluloses [22]. Most native cellulosic materials accordingly appear to contain cellulose molecules of approximately the same average molecular weight.

The chain-length distribution obtained for the hemp and jute celluloses is very similar to that found by an identical technique for ramie [21]. Cotton cellulose was previously found to have a D.P. distribution resembling that of flax; that is, with one maximum but with a pronounced left hand skewness [21]. The frequency distribution of the kapok is more similar to that of milkweed floss, both containing only one maximum and exhibiting right-hand skewness. This is a distribution quite different from that reported by Zapf [27] for a nitrated kapok cellulose, as referred to above. The first two peaks noticed by this author might have been the result of heavy degradation during the isolation of the cellu-

lose and to the presence of low molecular weight hemicelluloses. It would seem from the present results that the molecular weight distribution of native celluloses might vary to a certain extent from one material to another. While this is quite possible, more definite conclusions cannot be drawn at the present stage due to the very approximate nature of the fractionation methods used.

Experimental

Materials

Untreated jute fibers (*Corchorus capsularis*) were kindly supplied by Dr. A. K. Sanyal, Calcutta, India. Untreated Italian (soft) hemp (*Cannabis sativa*) and kapok (*Ceiba pentandra*) were obtained through the courtesy of Eastern Chemical Corporation, Newark, N. J. All fibers were extracted with ethanol-benzene (1:2 vol./vol.) and with cold water, after which they were stored in the air-dried condition in a cool, dark place.

Methods

α-cellulose, pentosan, lignin, and uronic anhydride were determined by standard methods as described elsewhere [22, 25]. The acetyl content was estimated by the method of Whistler and Jeanes [26]. After hydrolysis and separation by paper chromatography [22], the amount of each sugar was determined by the *o*-aminodiphenyl method [24].

Nitrogen determinations were carried out by a semimicro Kjeldahl procedure [22]. Intrinsic viscosities were measured as described earlier [22], corrected for variations in nitrate substitution [22], and converted to degrees of polymerization with the relationship of Newman, Loeb, and Conrad [15]:

$$\text{D.P.} = K[\eta]_{500}$$

where $[\eta]_{500}$ is the intrinsic viscosity in ethyl acetate as measured at a shear rate of 500 sec.$^{-1}$ and K is a constant, which in this case is approximately 80.

Nitrations were carried out with a mixture of nitric acid, phosphoric acid, and phosphorus pentoxide, as described in detail on several occasions [21, 22, 25]. For fractionation, 2.0 g. of nitrate was dissolved in 950 ml. of 93% aqueous acetone and precipitation induced by gradual removal of the solvent with air. Care was taken to obtain fractions of approximately the same size throughout. A total number of 20–30 fractions was obtained in each of duplicate experiments which checked reasonably.

Acknowledgment

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The Fine Structure of Keratin

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THIS article is a sequel to an earlier one [11], in which the connection between the cellular structure of animal hairs and their chemical heterogeneity was discussed. Hairs consist entirely of dried cells, in many of which the normally occurring constituents of living matter are still present in an altered form along with the extensive deposits of hardened keratin. The "cellular remnants," consisting of nuclei, cell membranes, and less well defined cytoplasmic inclusions, amount to about 10% of the dry weight of the fiber. These may be referred to collectively as the *non-keratins* to distinguish them from the principle constituent, the protein *keratin*.

The word "keratin" should not be regarded as a name for a single well defined substance, but rather for a class of intracellular proteins which have in common certain properties of insolubility, stability, and hardness due to a high content of the cross-linking amino acid, cystine. The keratin of the cuticle, for instance, differs from that of the cortex in not being fibrous; in the cortex itself, the fibrous keratin may differ in solubility and stability from cell to cell. When, as in wool and other curly and crimpy fibers, there is a relation between the fiber shape and the geometrical distribution of stable and less stable keratin, this type of heterogeneity assumes a particular importance in determining the behavior of the fibers [7, 8, 11].

In the present paper we wish to discuss the fine structure of the keratin itself, i.e., the structural details of a size smaller than can be resolved by the light microscope but larger than those responsible for the wide angle X-ray diffraction pattern (<10Å). Structures of this order (10–1000Å) are most easily studied electron-microscopically; our results were obtained by an application of the method of thin (or ultra) sectioning. It will be shown that at this level fibrous keratin may be considered to possess a duplex structure — a system of fine filaments (diameter ~60Å) held together by an amorphous cement. The fibrous elements may be more or less completely fused according to the amount of cement present.

Some of this work, particularly relating to the formation of keratin, has been described previously [3, 5, 14]. The present paper will be mainly concerned with its relevance to the structure of keratin itself, with special reference to wool.

Materials and Methods

The method of preparing thin sections (0.05–0.02μ) of biological materials for electron microscopy need not be described here, as it is already a standard procedure subject only to minor variations in different laboratories [16, 17]. We have imbedded and sectioned both fully hardened hair and wool (or derivatives of these) and partly formed hair in follicles of the skin. Fully hardened hair has not proved easy to section, and, unless chemically modified, the sections, when obtained, were not very informative. However, the fully formed but incompletely keratinized hair in the follicle is a more amenable material; it provided most of the results to be described below. Except in the case of the hardened hair, it was necessary to fix the material before imbedding. The hardened hair is, in a sense, already fixed, and fixation has some resemblances to keratinization. The only suitable fixative for the hair root is the buffered osmium tetroxide solution (1% OsO_4 at pH 7.2) described by Palade [16]. Buffered formaldehyde preserves many of the large scale structures, but is inferior to the osmium fixative for fine detail. The same conclusion has been reached by electron microscopists who have studied the fixation of other tissues [16].

Hair roots or wool roots were plucked, immersed immediately in the osmium fixative for periods of 2–4 hr., washed, dehydrated, and imbedded in methacrylate or epoxide polymers. With certain partly disintegrated derivatives of hair, a fixation in buffered formaldehyde solution (10% formaldehyde at pH 7) was satisfactory. Fiber fragments, e.g., from enzymatic disintegration or chemically extracted fibers, were fixed in formaldehyde solution for 24 hr., washed, dehydrated, and imbedded.

The electron microscopes used were a Siemens Elmiskop 1 and a Philips 100.

Results and Discussion

The Histological Level

Before proceeding to describe the new results of high resolution microscopy, it should be mentioned that the use of the electron microscope at low magnifications (<10,000×) has confirmed the findings of the earlier work [11] mentioned above, which was based on light microscopy. The cellular character of the hair or wool, which is usually difficult to appreciate in the light microscope, is immediately obvious in cross sections in the electron microscope. The cortex in cross section is seen as a condensed mass of cells whose faces meet in complicated reentrant or interlocking surfaces [14]. Since the cells are solid, these interlocking surfaces must contribute to the strength and coherence of the structure. The two cell membranes at each interface and the nuclear residues may also be seen.

The conclusion reached earlier [12] that the residues, after extraction of wool with alkalies (or after the extraction of oxidized wool with ammonia), consisted of cell membranes, nuclei, and other ill defined nonkeratins was confirmed by examining sections such as that shown in Figure 1, which shows this residue. The residue was previously described as a tubular structure placed between the cuticle and cortex [1].

Some new facts have emerged concerning the cuticle. That the cuticle possesses in effect a laminar structure — a very resistant external membrane (epicuticle), a keratinous layer (exocuticle), and an inner, nonkeratinous layer (endocuticle) — was deduced from an examination of fragments of disintegrated fiber some years ago [10, 13]. Sections of such fragments and also of extracted wool confirms these deductions and show that the inner layer (endocuticle) really consists of the modified remnants of the cellular apparatus proper to these cells [5]. The cell membranes of cuticle and cortex are insoluble in keratinolytic solvents for unknown reasons; the external cell membrane of the cuticle cells (epicuticle) appears thicker, more dense, and more in-

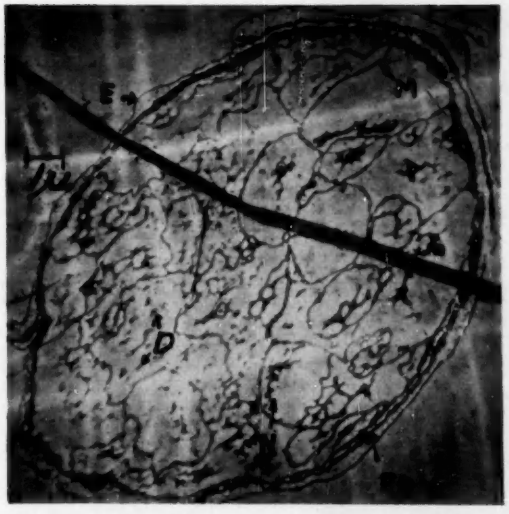

Fig. 1. An example of the use of the method of thin sectioning for electron microscopy to elucidate the results of the chemical extraction of a wool fiber. The fiber has been oxidized by peracetic acid and extracted with ammonia [1]. The keratin has been entirely removed; the residue consists of cell membranes *M*, nuclei *N*, and cytoplasmic debris *D*. The external membrane *E* of the cuticle cells, which forms the epicuticle, is somewhat more dense than the internal membranes. The cytoplasmic debris of the cuticle cells forms a well defined layer, the endocuticle *ED* (see Figure 2).

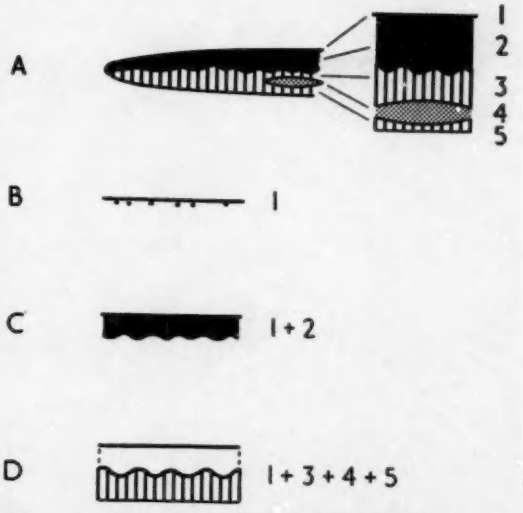

Fig. 2. The structure of the cuticle cell and of certain chemically extracted derivatives of that cell as deduced from thin sections. (*A*) portion of an intact cell showing (1) the external cell membrane (epicuticle), (2) the keratinized layer (exocuticle), (3) the inner layer (endocuticle) consisting of the condensed cellular apparatus which is not keratinized and is insoluble in keratinolytic solvents, (4) the nucleus, and (5) the inner cell membrane, (*B*) the membrane of the Allworden sacs, (*C*) the residue of the cuticle cell remaining after tryptic digestion, and (*D*) the cuticular residue remaining after the fiber, oxidized by peracetic acid, is extracted to remove the keratin [2].

soluble than the other membranes. It is evident that one of the changes occurring during the hardening of epidermal structures is a thickening and chemical modification of the cell membranes.

Figure 2 shows the relations of the several layers of the cuticle and certain cuticular derivatives as they appear in section, and is essentially the same as that deduced earlier [10]. It will be noticed that there is no layer between the cortical cells and the cuticle cells (i.e., no "subcutis" or "between membrane"). All the various sheetlike or tubular structures observed in chemically broken down hair can be accounted for in terms of the several layers of the cuticle itself or of the membranes of the cortical cells.

Fine Structure of Cortical Keratin

Within the cortical cells themselves are found the solid condensed mass of fibrous keratin whose detailed structure has previously been studied electron-microscopically by methods which involved the disintegration of the fiber into thin fragments. Such methods showed that fibrous units of two orders of size could be distinguished (see Review in [10] and [14]); large fibrils visible in the light microscope ($\sim 0.2\mu$ in diameter) and, within these, finer filaments approximately 100Å wide. A study of thin cross sections confirms these findings in essentials, but gives a much more complete and satisfactory view.

It has proved informative to compare cross sections at successive levels in the growing follicle which differ in the degree of consolidation of the keratin, in order to obtain an insight into the nature of one keratinization [5]. An example of such a section is given in Figure 3. A higher resolution micrograph of a portion of a field, such as that of Figure 3, is shown in Figure 4.

First of all, one notes the existence of the large fibrils (seen here in cross section) of a considerable range of size and of cross-sectional shape. The high

Fig. 3. An electron micrograph of a cross section of a hair in the upper keratinous zone of a human hair follicle, showing portion of the cortex. Two nuclei are seen at *N* and fibrils in cross section as at *F*. A cell membrane may be found at *M*. *P* is a pigment granule. *C* is the edge of the cuticle.

resolution micrograph (Figure 4) shows that the large fibrils are aggregates of smaller fibrils, which we shall refer to as filaments. A series of sections proceeding up the follicle [5] shows that in the final stages of growth the large fibrils, originally rounded in section, condense to give more massive aggregates of a variety of cross-sectional shapes with a marked tendency to lateral adhesion, forming thick sheets. This process remains incomplete in the final fiber, being impeded by the cytoplasmic apparatus of the cell (Figures 3 and 4) which remains between the fibrils.

In wool fibers the lateral fusion of the fibrils is greater on the paracortical side than on the orthoside, which probably accounts for the differences in stability and penetrability of the two segments [14], as shown in Figure 5*a*.

An examination of cross sections of fibrils at high resolution shows that one may distinguish two components which, in Figure 4, are seen as (*a*) the light dots, i.e., cross sections of filaments ~60Å in diameter, and (*b*) a darker ground substance between the filaments which are spaced some 80Å apart center-to-center. We interpret this image as evidence that the filaments are imbedded in or cemented together by a second component which is not fibrous in texture and scatters more electrons than the filaments themselves. The origin of contrast in electron micrographs of fixed tissues, i.e., the cause of differences in electron scattering power, is still under discussion. However, we may be fairly certain of the cause in this instance, because in keratin we have a protein which, because of its high content of cystine (or cysteine), reacts with the osmium tetroxide of

Fig. 4. A higher magnification of a portion of Figure 3 to show the fine structure of the fibrils *F*. Several fibrils are fused laterally. Within the fibrils may be seen the closely packed α-filaments. These appear as light dots on a darker ground, which represents the more dense γ-cement (see text and Figure 5). *M* is a cell membrane; *D* is cytoplasmic debris.

the fixative, leading to strongly electron scattering deposits of the lower oxides of osmium in the cystine-rich regions. In brief, the osmium is an "electron-stain" for cystine. The fact that the interfilamentous material is more dense than the filaments must mean, therefore, that there is more cystine in the cement than in the filament themselves.

We are thus led to the filament plus cement model for the fine structure of keratin, which has already been suggested on other grounds [1, 10, 13]. In Figure 5*d* this model is shown diagrammatically. The filaments are the fibrous units of the complex and must be the structures responsible for the wide angle X-ray diffraction pattern (the α-pattern) studied by Astbury and his collaborators [2]. These units may be referred to as α-filaments for this reason.

The cement is probably a protein of different composition from the filaments, particularly in respect of the frequency of cystine residues, which may be as high as 1 in 2 or 3. Its extensively cross-linked character possibly explains why it is not fibrous. Keratinization would thus seem to be a process whereby an insoluble complex is formed by imbedding a system of rather soluble filaments in a very insoluble cement. Degrees of keratinization can be conceived to arise from differences in the amount of cement present. Where the keratinization is more extensive, e.g., in the paracortex of wool fibers, the amount of the cement protein is probably increased, leading to a somewhat higher sulfur content.

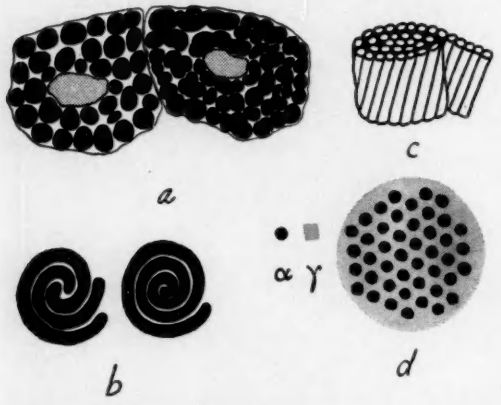

Fig. 5. A diagram to illustrate the structural features of cortical keratin as described in the text. (*A*) two cortical cells from wool in cross section showing nuclei and fibrils. On the left is an ortho-type cell in which the fibrils remain separate. On the right is a para-type cell in which an extensive lateral fusion of the fibrils has occurred. This situation prevails in human hair, (*B*) two modes of arrangements of the spiral structures within the fibrils seen in cross sections of hair (See Figure 6), (*C*) suggested twisted arrangement of the filaments in a fibril which can lead to appearances such as *B* in cross section and which can unroll and lead to sheets of filaments, and (*D*) the "filament plus cement" model for fibrous keratin. The α-filaments (large dots, diameter about 60Å) are imbedded in a sulfur-rich cement (fine dots—γ).

Chemical Extraction of Keratinized Fibers

This model is of value in explaining what might be expected when attempts are made to dissolve keratin. Assuming all the cystine cross-linkages are broken, one may expect to obtain derivatives of both filaments and cement. This seems to be the case when peracetic acid used to oxidize the cystine, as has already been suggested by Alexander [1]. Other solvents may extract more or less of the two components in various states of breakdown, but in any case an electron microscopic study of thin sections of the extracted material (Figure 1 is an example) would be necessary to reveal the precise nature of the attack. This kind of collaboration between electron microscopist and chemist seems essential in further work on the composition of all heterogeneous fibers.

The Organization of the Fine Filaments Within the Fibrils

In the center of the fibrils shown in Figure 5 it will be seen that the filaments are packed in an approximately hexagonal array; in other areas, particularly towards the edges of the fibrils, they appear to be arranged in a series of parallel rows, and the individual filaments are hard to make out. In micrographs, such as Figure 6, spirals and whorls may be seen clearly. These structures, which are not clearly developed in earlier aggregates of filaments formed lower down in the follicle, appear to be a form of consolidation of the structure brought about by the adhesive effect of the interfilamentous cement. The reason why rows or lines of filaments are seen rather than single filaments is not immediately obvious, nor do longitudinal sections clear the matter up. A likely explanation is that, where whorls are seen in cross section, the fibrils are also slightly twisted around their long axis. When cross-sectioned (see Figure 5*c*), only those filaments which are nearly at right angles to the section will be seen end on; they will appear as dots; others will be tilted to the plane of the section; their images will partly fuse and appear as parallel lines. Twisted fibrils have in fact

been observed in disintegrated wool [15] and in longitudinal sections of follicles.

These whorl formations sometimes reduce to rather regular spirals, but more often the geometry is less ideal and adjacent fibrils fuse extensively. The drawings in Figure 5 show some of the characteristics observed. One is reminded of the spiral structures observed on the surfaces of crystals, which are attributed to growth patterns centered around dislocations in the crystal lattice. Possibly the origin of spirals and whorls will be found in similar defects in the packing of long filaments. The filaments may at first pack in a quasi-hexagonal pattern, as in the tactoids of tobacco mosaic virus. However, this regularity could scarcely persist for long. The filaments, one supposes, are not perfectly rigid, and slight defects would be introduced. In later stages it would seem more likely that further filaments (and the adhering cement) would be added as suggested in Figure 5*b*, which would lead to the growth of spirals of one or more arms.

A further possibility, not easy to test, is that the adhesion among the individual filaments is greater in the tangential direction than in the radial. This possibility is suggested by the results of Jeffreys, Sikorski, and Woods [9], who find that certain disintegrative procedures break the keratin into sheets rather than into bundles of filaments. Disintegration could produce either fibrous bundles or sheets, resulting from an unrolling of the "scrolls" (Figure 5*c*), according to the treatment.

Summary

1. The application of the technique of cutting thin sections for electron microscopy to the problem of the structure of hair and wool confirms the earlier views obtained by disintegration methods as summarized in the Review by Lindberg et al. [10].

2. Both cortex and cuticle are cellular and the normal constituents of biological cells are still present in a dried and altered form, along with the intracellular deposits of keratin in the final hair.

3. The cell membranes are fused together and chemically altered in such a way as to be insoluble in keratinolytic solvents. They are therefore left as a residue when the keratin is extracted. Nuclei and certain cytoplasmic residues have also become insoluble in such solvents.

4. The outer cell membrane of each cuticle cell is particularly thick, dense, and insoluble, and constitutes the special membrane referred to as the epicuticle. Within the cuticle cell the contents are laminated: an outer (nonfibrous) layer of keratin and an inner layer, a residue of the cell apparatus which, although very insoluble, is not keratin.

5. The fibrous keratin of the cortical cells consists of condensed bundles or fibrils of fine filaments (α-filaments, width ca. 60Å). Further, the large bundles (or fibrils) may be extensively fused laterally to give massive irregular aggregates (0.05–0.2μ).

6. This condensation is more extensive on the para side of wool fibrils than on the ortho (outer face of crimp wave), and explains the greater insolubility of the paracortex.

7. The α-filaments are held together in the fibrils by a cement which does not appear to be fibrous and has a higher cystine content than the filaments. The same cement holds the fibrils together when they fuse into aggregates.

8. The protein of the cuticle is not fibrous and appears to bear some resemblance to the cement substance of the cortex.

Acknowledgments

Much of this work was carried out in collaboration with Mr. M. S. C. Birbeck, to whom the writer is most grateful for permission to reproduce several

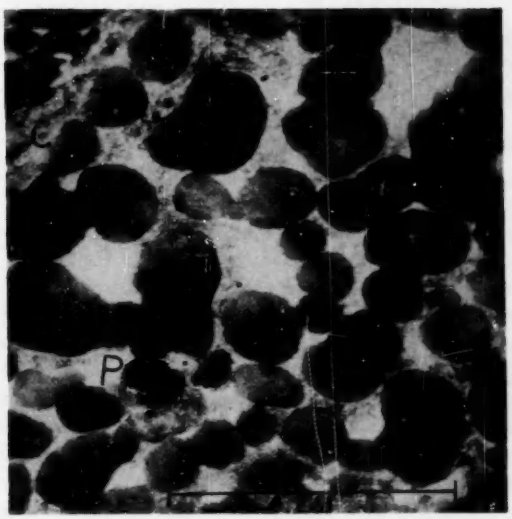

Fig. 6. Cross section of the cortex prior to the final condensation, showing the spiral arrangement of the filaments within the fibrils. A similar appearance is produced in the final hair if it is reduced and stained with the osmium fixative. *C* is the edge of the cuticle; *P* is a pigment granule.

micrographs which have appeared in a joint paper. The photography is the work of Mr. K. Moreman and Mr. M. Docherty, to whom the writer is much indebted.

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Molecular Organization in Keratins

Part III: The Densities of Physically and Chemically Modified Wools

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Abstract

A series of density determinations on physically and chemically modified wools shows that extensions up to 70% and supercontraction of 15% in steam are not accompanied by density changes. In contrast, residues from chemical extractions and enzymatic digestions show significant increases. Cortical cells fractionated from trypsin digests by gradient column techniques have densities comparable to that of porcupine quill tips. The extent to which these measurements may be correlated with crystallinity is discussed.

Introduction

In Part II of this series [12], changes in the densities of native keratins were ascribed to differences in the content of crystalline material. Although this concept has proved satisfactory when applied to simple polymers [27, 28], its quantitative application to keratins is complicated by gross heterogeneity at both the molecular and histological levels of organization. Further information on the histological distribution of the crystalline material in wool and the effect of its complex molecular structure was sought by measuring the densities of a series of physically and chemically modified wools. These results are described in the present contribution.

Experimental

The material used in the present work was 64's quality virgin Merino wool which had been hand-picked to remove vegetable and other impurities and successively extracted with cold petroleum ether, ethanol, and distilled water. After chemical or physical treatment, the samples were thoroughly dried and densities measured by flotation in mixtures of dry bromobenzene and *o*-dichlorobenzene as described in Part II.

Extension and Supercontraction

Fiber bundles were extended in steam during a period of about 30 min. to the required extension, steamed for a further 30 min., and washed in cold water; the degree of set was measured after drying in a desiccator. X-ray diagrams obtained from the fiber bundles showed that even at 70% final set the α–β transformation was not complete, probably due to the short setting period in steam. Prolonged steaming was deliberately avoided in order to minimize chemical degradation of the fiber.

A supercontraction of about 15% was obtained by rapidly extending a fiber bundle in cold water to 50% extension, steaming for 2 min., and then steaming for a further 30 min. after removing the load.

Acid Hydrolysis

A sample of 20 g. of wool was shaken for 70 hr. in 2 l. of 6 *N* HCl at 28° C., the residue being filtered off, washed, and dialyzed against running tap-water for 24 hr. Microscopical examination showed the residue to consist of individual cortical cells and scales, together with long strands of cortical cells. It was found that the cell strands (Fraction A) were retained when the residue was passed through several layers of cheesecloth. Traces of cell strands were removed from the filtrate by repeating the process several times, yielding a preparation of individual cortical cells and scales (Fraction B).

Alkaline Thioglycollate Extraction

Samples of a residue obtained after extraction of wool with 1 *M* sodium thioglycollate (pH 10.5) at

50° C. for 1 hr. and prolonged washing in water, and kerateine 2, a purified protein extracted from wool with alkaline thioglycollate solutions [15], were kindly supplied by Dr. F. G. Lennox and Mr. J. M. Gillespie. In both cases the starting material was Merino 64's commercial top.

Enzymatic Hydrolysis

The preparation of wool cells was attempted by swelling in 0.1 *M* sodium caprate solution, pH 11.0 [7] and digesting in 0.1% crystalline bovine chymotrypsin (Armour) for 6 da. at 25° C. The enzyme was dissolved in 0.1 *M* phosphate buffer, pH 7.0, containing 0.01% merthiolate with a wool/liquor ratio of 1/100. The extent of digestion was not sufficient, however, to reduce the bulk of the wool to cells; this was subsequently achieved by using 5% crude trypsin (Pfanstiehl) in 0.1 *M* borate buffer, pH 8.4, at 25° C. with the same merthiolate concentration and wool/liquor ratio. The wool was transferred to a fresh enzyme solution every 24 hr., and after 5 da. could be largely reduced to cells by shaking gently with glass beads.

A fractionation of the cells was obtained by means of density gradient columns [18, 29] containing mixtures of carbon tetrachloride and ethanol, with a density range of 1.25 to 1.33 g.cm.$^{-3}$. The attainment of equilibrium was accelerated by centrifugation; the separation at equilibrium is illustrated in Figure 1. Samples of the three layers were withdrawn by means of a hypodermic syringe and examined microscopically. Layer 1 was found to consist of fiber fragments, Layer 2 of cortical cells, and Layer 3 of cuticle fragments.

Fig. 1. Diagram illustrating the separation of three fractions from a trypsin digest of wool by means of a density gradient column. (1) fiber fragments; (2) cortical cells; (3) cuticle fragments.

In addition to the preparation of wool cells, enzymatic hydrolysis was used to produce a series of residues in which the extent of degradation varied from slight to practically complete dissolution. Samples of wool were digested for periods of 24 hr. and 48 hr. with 1% crude pepsin (Difco 1:10,000) solution buffered at pH 1.8 with 0.25 *M* glycine and 0.25 *M* NaCl. Digestion was also carried out with 1% ficin (Delta) solution, 1% crude trypsin (Pfanstiehl) solution, and 1% crude papain (Doward) solution; each was buffered at pH 8.0 with 0.1 *M* sodium borate. In each case the solutions were made 0.1 *M* with respect to thioglycollic acid to assist the action of the enzyme; a few drops of toluene were added to inhibit the growth of micro-organisms. The digestions were carried out at 40° C. with a wool/liquor ratio of 1/100; percentage digestion was calculated on a dry weight basis relative to further samples incubated with buffer and thioglycollate in the absence of enzyme.

Results and Discussion

In Part II the interpretation of density variations between different α-keratins was based on the simple concept of a variable content of crystalline material. In view of the heterogeneity at the histological level, however, it is of considerable interest to examine the distribution of crystallinity within the wool fiber. As mentioned previously, an increase in density will, for the purposes of the present discussion, be taken as indicating an increase in crystallinity.

In addition to the histological complexity, account must be taken of the existence of a second crystalline form, designated β-keratin [4]. Even with the simplest concept of crystallinity it is necessary to distinguish four phases: α-crystallites, β-crystallites, noncrystalline material in which the chains are folded and intramolecularly hydrogen bonded, and noncrystalline material in which the chains are extended and intermolecularly hydrogen bonded. Although there is no evidence for β-crystallites in the X-ray diffraction diagrams of hair or wool, absorption bands characteristic of the extended configuration have been observed in the infrared spectra of both materials [9, 11], and it has been concluded that a small amount of the noncrystalline extended phase is present.

Extension and Supercontraction

An attempt was made to obtain further information on the contribution of the extended phase by studying changes in the density of Merino wool when stretched in steam. In this process the α-crystallites are destroyed and β-crystallites created [4], and changes in crystalline content should be accompanied by density variations, particularly if d_c differs for α- and β-crystallites. The results given in Table I show that, up to 70% extension, the density change scarcely exceeds the experimental error. Provided that the crystalline content is not so small that major variations would give rise to only small density changes, this lends some support to the conclusion of Astbury and Woods [4] that the densities of crystalline α- and β-keratin are not very different. If this is true, it follows from the constancy of the density during extension that the fraction of crystalline material remains roughly constant; that is, β-crystallites are formed at about the same rate that α-crystallites are destroyed [5].

Supercontraction in steam, if accompanied by a decrease in crystallinity, might be expected to result in a decreased density. Woods [31] observed the diameter increase accompanying supercontraction, concluding that the change in density was not very great; our density determination at 15% supercontraction (given in Table I) confirms this. It appears, therefore, that some degree of supercontraction is possible without destroying the crystallinity, a conclusion which Astbury [2] had previously considered on the basis of X-ray diffraction studies.

Enzymatic Hydrolysis

In general, the crystalline regions of biological high polymers are less readily digested by hydrolytic enzymes than the noncrystalline regions by virtue of the cooperative effect of the longitudinal and lateral cohesive forces [19]. In the case of silk, for example, the rate of hydrolysis with pepsin is sufficiently different in the two phases to enable crystalline material to be isolated by this means [8]. Keratins, however, are characterized by an extreme resistance to hydrolysis with proteolytic enzymes, due partly to an extensive three-dimensional network of disulfide linkages [14]; any differences in cystine content between crystalline and noncrystalline regions might be expected to affect their relative rates of digestion.

In the present work, proteolytic enzymes were used to obtain cell preparations, so that the crystallinities of the histological components could be investigated, and also in an attempt to isolate material enriched in crystalline phase. In the latter case the digestion was accelerated by the addition of a reducing agent, which to some extent compensated for any differences in the concentration of disulfide linkages in the two phases. The results of these experiments are summarized in Tables II and III.

The slight decrease in density after swelling in sodium caprate is in accord with the view of Crewther [7], who considers that some denaturation of the intercellular material takes place during this treatment. Partial removal of this material with

TABLE I. Densities of Extended and Supercontracted Samples of Merino Wool

Treatment	Density (g. cm.$^{-3}$)
Nil	1.302
Heated in water at 100° C. for 1 hr.	1.302
Extended in steam, set at 20% extension	1.300
Extended in steam, set at 50% extension	1.300
Extended in steam, set at 65% extension	1.298
Extended in steam, set at 70% extension	1.300
Supercontracted ca. 15% in steam	1.303

TABLE II. Densities of Residues from Enzymatic Hydrolysis of Merino Wool

Treatment	Density (g. cm.$^{-3}$)
Nil	1.302
Swollen in sodium caprate at pH 11.0	1.298
Digested 6 da. in chymotrypsin after swelling	1.307
Digested 5 da. in crude trypsin after swelling	1.329
Fraction 1 from trypsin digestion (fiber fragments)	1.307
Fraction 2 from trypsin digestion (cortical cells)	1.327
Fraction 3 from trypsin digestion (cuticle fragments)	1.321

TABLE III. Densities of Residues from Enzymatic Hydrolyses of Merino Wool in the Presence of 0.1 *M* Thioglycollic Acid

Treatment	Duration (days)	Digestion (%)	Density (g. cm.$^{-3}$)
Control pH 1.8	1	—	1.306
Control pH 8.0	1	—	1.305
1% crude pepsin pH 1.8	1	54	1.320
	2	73	1.330
1% crude papain pH 8.0	1	75	1.324
	2	85	1.322
1% crude ficin pH 8.0	1	25	1.311
	2	46	1.323
1% crude trypsin pH 8.0	1	17	1.308
	2	14	1.309

chymotrypsin leads to a small but significant increase in density, which may be attributed either to the removal of low density protein or to an increased accessibility of voids in the histological structure. In untreated wool, these voids are accessible to certain dye molecules when the fiber is swollen in aqueous solutions [3, 23, 26]; in the dry condition it is probable that some degradation of the intercellular material is necessary before they become accessible to organic solvents of the type used in these measurements.

As is the case in most enzymatic hydrolyses of wool, the extent of attack by trypsin varied considerably from fiber to fiber. In order to investigate the densities of the histological components, fractionation was essential. Samples were taken from the density gradient columns at the positions indicated in Figure 1 and designated Fractions 1, 2 and 3. The densities are given in Table II; it will be seen that the density of Fraction 3 is slightly less than that of Fraction 2, despite its lower position in the carbon tetrachloride-alcohol gradient column. This would indicate a greater accessibility of Fraction 2 to ethyl alcohol.

Upon microscopical examination, Fraction 1 was found to consist of fiber fragments similar in appearance to those obtained after treatment with chymotrypsin. A small amount of intercellular material appeared to have been removed, resulting in the same increase in density as observed with the chymotrypsin treatment.

Fraction 2 consisted of cortical cells; the measured density, 1.327, lies between the values reported earlier [12] for porcupine quill tips and echidna quill tips. The complete removal of intercellular material and partial removal of interfibrillar material from the cortex of wool leads therefore to a density, and presumably crystallinity, of the same order as the most crystalline α-keratins known. Woods [31] suggested that the crystalline fraction of wool is largely concentrated in the cortical cells; present evidence supports this view.

From the high value of the cortical cell density, it may be inferred that the intercellular material is considerably less dense, hence less crystalline. This is in accord with such evidence as the intercellular deposition of polymers [17, 21], the susceptibility of the intercellular material to enzymatic and acid hydrolysis [30, 31], its affinity for dyes [13, 24], and its ease of swelling [1].

A striking feature of the fractionation obtained in the density gradient column was the resolution of the layer designated Fraction 3, which consisted entirely of cuticle fragments. The enzyme resistant layer of the cuticle was for many years supposed to be the endocuticle [16], but the advent of ultrathin sectioning techniques has enabled the exocuticle to be identified as the enzyme resistant layer [22]. The cuticle fragments constituting Fraction 3 probably consist mainly of exocuticle together with epicuticle, which is also enzyme resistant. The unknown chemical composition of the epicuticle complicates interpretation of the measured density, 1.321, which might otherwise have been interpreted as indicating an enhanced crystallinity. If the exocuticle does, in fact, contain a proportion of crystalline material comparable to that of the cortical cells, the crystallites must be randomly oriented, as the cuticle gives a very poor X-ray diffraction diagram [4, 31] and is practically nonbirefringent [24, 31].

The densities of a series of residues obtained from wool after digesting with pepsin, papain, ficin, and trypsin in the presence of reducing agent are given in Table III. In every case, the density is greater than that of the controls; in Figure 2 the residue densities are correlated with the extent of digestion.

The initial mode of attack on the fiber appears microscopically similar with each of the four enzymes, leading to the release of cortical cells, but later the mode of breakdown varies according to the particular enzyme used. Despite this, however, there appears to be a significant correlation between density increase and extent of digestion, presumably due to the progressive removal of noncrystalline material.

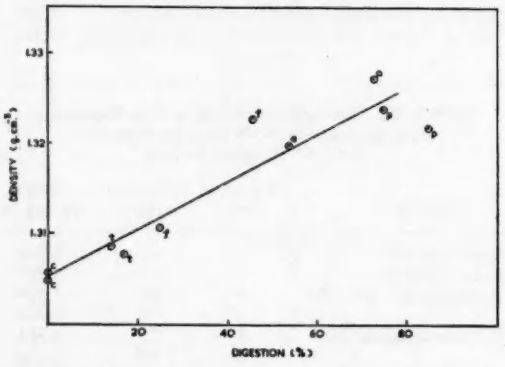

Fig. 2. Correlation of density and extent of digestion after various enzyme treatments in the presence of 0.1 *M* thioglycollic acid. *C*, controls; *t*, trypsin; *f*, ficin; *p*, pepsin; *a*, papain.

Acid Hydrolysis

The densities of the fractions isolated from wool partially hydrolyzed with hydrochloric acid are given in Table IV; Fraction A probably corresponds to a residue derived from the *p*-cortex and B to cortical cells from the *o*-cortex together with cuticle fragments. As with the enzymatic hydrolyses, the residues are considerably more dense than native wool, as might be expected if a preferential attack on noncrystalline material had occurred. The situation is complicated, however, by the fact that certain amino acids (for example, aspartic acid) are preferentially liberated during hydrolysis while cystine is released only slowly [6]. It is not difficult to visualize a stage in the hydrolysis where the residue may contain fragments of polypeptide chains loosely knit by occasional disulfide linkages. In this condition the residue would probably be permeable to the organic solvents used in these measurements; the measured density would be very high, ultimately approaching the value calculated from the amino acid composition [20].

Extraction with Alkaline Thioglycollate

Both the material remaining after alkaline thioglycollate extraction and the purified extract have densities considerably in excess of untreated wool. To what extent the increased densities may be associated with increased crystallinities is uncertain. However, the purified extract has been shown to cast from solution into the folded configuration [10], and may well be derived from the more crystalline regions of the wool fiber. How far the increased density of the residue is associated with an increased accessibility to solvent molecules is uncertain at present.

General Conclusions Regarding Density and Crystallinity in Keratins

Of the various methods which have been used to investigate crystallinity in polymers, the X-ray diffraction method is perhaps the most direct, although it is also the most difficult to apply quantitatively. X-ray diffraction diagrams obtained from the various native α-keratins investigated in Part II show a considerable variation in definition; if the crystallite sizes are not greatly different it may be concluded that considerable variation in crystalline content occurs.

TABLE IV. Densities of Chemical Degradation Products of Merino Wool

Treatment	Density (g. cm.$^{-3}$)
Nil	1.302
Residue from hydrolysis with 6 *N* HCl for 70 hr. at 28° C.	
Fraction A (cortical cell strands)	1.331
Fraction B (cortical cells and cuticle fragments)	1.317
Residue after 1 hr. at 50° C. in 1 *M* thioglycollate, pH 10.5	1.331
Purified extract (kerateine 2)	1.323

The close parallelism between the densities of horn (1.28), wool (1.30), and porcupine quill tip (1.32) and the definitions of their respective X-ray diagrams provides rather direct evidence that a variation of density with crystallinity, so well established in simple polymers, also occurs in α-keratins. In general, the results of the present investigation support this conclusion insofar as the removal of intercellular and interfibrillar matrix leads to the expected increase in density. It is difficult, however, to reconcile the increase in density of both kerateine 2 and the material resistant to alkaline thioglycollate extraction without invoking the notion of an increased accessibility to solvent molecules.

It appears, therefore, that the possibility of obtaining quantitative estimates of crystallinity from density measurements may be restricted to native keratins and to keratins modified by processes which do not involve extraction. Until such time as reliable estimates of the effective crystalline and noncrystalline densities of keratin can be made, the method must remain semiquantitative at best.

At present there is insufficient information to decide with certainty how far differences in amino acid composition will affect crystallinity comparisons by the density method. It is unlikely that the effect will be as great as in the regain and deuterium exchange methods; it is not anticipated that minor compositional differences, for example, between different wools will be important. The observed density of human hair (1.317) would indicate a crystallinity comparable with that of porcupine quill tip; while the definition of the X-ray diagram is better than wool ($d = 1.302$), it is certainly not as good as quill tip. This is probably a case where a gross difference in chemical composition must be taken into account, for the cystine content of hair is very much greater than that of either wool or quill tip. The specific volume of the cystine residue

is considerably less than average [20]; as there is no corresponding decrease in the proportion of residues of comparably low specific volume [25], the density might be expected to be disproportionately high, as appears to be the case.

Although the density is clearly influenced by existing differences in chemical composition, estimates of relative crystallinity based on density are probably less affected by minor differences in composition than estimates obtained from sorption and deuterium exchange measurements. Further, assumptions concerning the sorption mechanism and the relation between accessibility and crystallinity are avoided.

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The Nonaqueous Carboxymethylation of Cotton

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Abstract

Cotton fiber, thread, and fabric were carboxymethylated by a nonaqueous process. Activated cotton was impregnated with an isopropanol solution of monochloroacetic acid and refluxed with 0.3% sodium hydroxide in a mixture of methanol and isopropanol. Degrees of substitution ranging up to 0.09 were achieved. Higher values can be obtained by retreatment or premercerization.

Four varieties of cotton fiber have been carboxymethylated by this method. Correlation between the reactivity and the original physical properties of the fibers has been shown.

Textile properties of fabric treated by this nonaqueous method and those of a sample treated by the usual aqueous alkali method were compared at equal substitution.

The α-methyl-, α-ethyl-, α-propyl-, α-decyl-, and α-cetylcarboxymethyl derivatives of cotton were prepared in low degrees of substitution, using the appropriate α-halocarboxylic acid as etherifying agent in the nonaqueous reaction.

Introduction

Chemical modification of cotton has long been one of the principal activities of this Laboratory [5, 6]. Many useful properties, both new and novel, have been introduced into cotton products with retention of the valuable fibrous form of the fiber.

Partially carboxymethylated cotton, one of the research products which has been investigated at considerable length [1–4, 12–14], has been prepared by the action of monochloroacetic acid on cotton in the presence of a large excess of 30–50% aqueous alkali. The new functional group thus introduced imparts changed dyeing properties, increased swellability and absorbency, cation exchange properties, and soil resistance, and acts as a built-in catalyst for the condensation of methylol resins.

A recent publication by Walecka [17] has described a new method for the partial carboxymethylation of cellulose. By this method, wood pulp was impregnated with an isopropanol solution of monochloroacetic acid, followed by treatment of the pulp by refluxing with a methanol-isopropanol solution of sodium hydroxide. The alkali used was only in an amount sufficient to neutralize the monochloroacetic acid picked up by the pulp and yield an excess concentration of 0.3%. Low degrees of substitution, in the range of 0.006 to 0.062, were achieved. Products so made were investigated as base material in the manufacture of paper.

When this nonaqueous carboxymethylation was contrasted with the method utilizing a large excess of concentrated aqueous alkali, the possibility of differences in the products was evident. The method of Walecka was easily adapted to the treatment of cotton fiber, yarn, and fabric. Moreover, use of other α-halocarboxylic acids in place of monochloroacetic acid resulted in cottons bearing alkyl substituents alpha to the carboxyl group of the ether substituent.

Experimental

Effect of Monochloroacetic Acid Concentration

Using conditions similar to those described by Walecka [17], the effect of increasing concentration of monochloroacetic acid was investigated. For this experiment, samples of 12/5 cotton sewing thread previously purified by extraction with monoethanolamine were used [9]. Skeins were boiled in water to activate the cellulose; then the water was removed by exchange with three portions of anhydrous methanol, followed by three changes of anhydrous benzene. The activated skeins were soaked in isopropanol solutions of monochloroacetic acid (0.5–30%) for 30 min. and the takeup adjusted to about 100%. These acid impregnated skeins were then treated at

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reflux for 1 hr. with a solution of sodium hydroxide in 12.5% methanol–87.5% isopropanol. The alkali was used in an amount sufficient to neutralize the acid and yield an excess concentration of 0.3%. After the reflux treatment, the skeins were removed, washed with water, soured with dilute acetic acid, and thoroughly washed again with water.

Figure 1 shows a plot of the degree of substitution (DS) obtained against concentration of the monochloroacetic acid solution used. It is evident that substitutions in excess of 0.075 (or about 1 ether substituent/15 glucose residues) are not economically feasible by increase of concentration alone. Above a concentration of 5%, and up to 30% acid, no appreciable increase in DS is obtained which compares with that achieved by a simple retreatment procedure. For example, a double treatment with 5% monochloroacetic acid gave a product with a DS of 0.10.

The DS of these and subsequent samples was determined through a measure of the carboxyl content of the derivatives. For this determination, samples were acidified by soaking in a 2% aqueous solution of hydrochloric acid for 4 hr., washed free of the mineral acid, and dried. Weighed samples of the acidified derivatives were placed in flasks with 100 ml. of distilled water and an aliquot of standardized 0.1 *N* sodium hydroxide solution added. The flasks were stoppered and allowed to stand for 2 hr. with occasional shaking. The residual sodium hydroxide was then back titrated with standardized 0.1 *N* hydrochloric acid to the phenolphthalein end-point. The carboxyl content was calculated and the DS estimated from the following equation:

$$DS = \frac{(162)\ (\%\ COOH)}{4500 - (R)\ (\%\ COOH)}$$

where R is the molecular weight of the ether substituent minus one, i.e., 58 for carboxymethylcellulose.

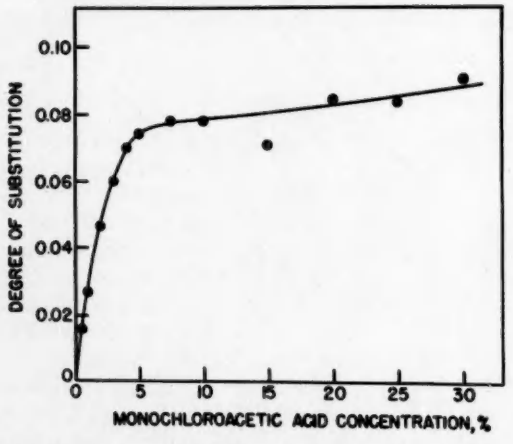

Fig. 1. Change of DS with concentration of monochloroacetic acid.

Breaking strength, elongation at break, and thickness of the treated threads were determined by standard methods of testing and compared with the untreated and control in Table I. The results indicate a loss of strength as the DS increases, with little effect on the elongation at break of the thread. Thickness of the thread is increased. Moisture regain of the samples as determined at 70° F. and 65% relative humidity is also shown in Table I; this property also increased with increasing substitution. This change may be attributed to the substituent carboxyl groups without the complicating effect of mercerization which occurs in the aqueous alkali method of carboxymethylation.

Effect of Pretreatment

With the nonaqueous method of carboxymethylation, pretreatment of cotton is of extreme importance. As stated previously, the results of Table I and Figure 1 were obtained on ethanolamine-extracted cotton activated by a water boil and solvent exchange. With no activation pretreatment, the purified thread gave a DS of only 0.012 on treatment as above with 5% monochloroacetic acid. Mercerized thread similarly treated gave a DS of only 0.013, but, when the mercerized thread was activated by the water boil followed by solvent exchange, a DS of 0.107 was obtained by the carboxymethylation treatment. A higher DS, 0.115, was obtained on a skein of ethanolamine extracted thread which was mercerized, washed, soured with dilute acetic acid, thoroughly water washed, and solvent exchanged free of water with anhydrous methanol and benzene prior to carboxylmethylation with 5% monochloroacetic acid. This method of activation is one of the most effective pretreatments for the preparation of cellulose derivatives.

Effect of Varietal Differences of Cottons

A number of researchers have pointed out differences in the rate and extent of chemical modification

[2] The mention of trade names and firms does not imply their endorsement by the Department of Agriculture over similar products or firms not mentioned.

of cottons due to innate varietal differences [7, 8, 10, 11, 15, 16]. Such differences exert their effect on carboxymethylation, also. Four cottons used in a study of the effects of carboxymethylation by the aqueous method [8] were obtained and treated by the nonaqueous technique under fixed conditions. Samples of the raw fiber were activated by the water boil and solvent exchange pretreatment, then carboxymethylated with 5% monochloracetic acid. Results are shown in Table II. Rank correlation of the DS obtained with a number of the physical properties was investigated. The Spearman Rank Correlation Coefficient of the DS with the Micronaire [2] fineness, linear density, crystallinity, and maturity is shown in the table. The high rank correlation of DS with Micronaire fineness is in agreement with conclusions drawn from a similar study on the cyanoethylation of cotton [15]. Good rank correlation with linear density and crystallinity was also observed.

Comparison of the Textile Properties of Cottons Carboxymethylated by the Aqueous and Nonaqueous Methods

Samples of 48×48 boiled and bleached cotton sheeting were carboxymethylated (a) by the nonaqueous method, activating with a water boil fol-

TABLE I. The Effect of the Nonaqueous Method of Treatment on the Properties of Partially Carboxymethylated Cotton Threads

Treatment: % monochloroacetic acid	DS*	Breaking strength, lb.	Elongation at break, %	Thickness, in.	Moisture regain, %
0 (untreated)	—	10.2	12.2	0.0286	7.0
0 (control†)	—	9.7	12.5	0.0302	7.0
0.5	0.016	8.8	10.5	0.0291	7.2
1	0.026	9.1	11.9	0.0301	7.1
2	0.045	7.5	10.8	0.0300	7.3
3	0.060	7.3	10.5	0.0300	7.3
4	0.070	7.7	10.8	0.0304	7.3
5	0.074	8.0	11.9	0.0322	7.4
7.5	0.078	7.2	9.8	0.0298	7.5
10	0.078	8.2	10.9	0.0308	7.9
15	0.071	7.8	10.8	0.0302	7.9
20	0.084	6.8	10.7	0.0314	7.5
25	0.083	6.6	11.2	0.0327	8.1
30	0.091	6.6	11.4	0.0333	8.1

* Corrected for the carboxyl content of the control.

† Sample given the activation water boil, solvent exchanged, treated with 0.3% methanol–isopropanol solution of sodium hydroxide at reflux for one hr., washed, and dried.

TABLE II. Correlation of Degree of Substitution with Varietal Differences on Nonaqueous Carboxymethylation of Cotton Fiber

Variety of cotton	DS*	Micronaire fineness, Upland Scale	Linear density, grex	Crystallinity, %	Maturity, %
Rowden 41B	0.022	6.07	2.55	80	90
Delta Pine 14	0.024	4.36	1.88	80	79
Stoneville 2B	0.030	4.03	1.90	78	80
SXP	0.042	3.85	1.42	72	86
	ρ_{DS}†	−1.00	−0.80	−0.85	−0.40

* DS obtained on treatment of the activated solvent exchanged fiber with 5% monochloroacetic acid and 0.3% excess concentration of sodium hydroxide in methanol–isopropanol at reflux for 1 hr.

† Spearman Rank Correlation Coefficient, ρ, calculated from the formula: $\rho = 1 - \frac{6\Sigma d^2}{n(n^2-1)}$, where n is the number of pairs being compared and d is the difference in rank between a pair of values. In the event of ties, intermediate values are assigned, *i.e.*, in the event of a tie for 2nd and 3rd place, both are assigned a rank value of 2.5. The correlation shown, ρ_{DS}, compared the rank of DS obtained with the rank of physical properties indicated in the table.

lowed by solvent exchange through methanol and benzene, and treatment with 5% monochloroacetic acid and 0.3% excess sodium hydroxide solution, and (b) by the aqueous alkali method, padding to an 80% pickup of aqueous 10% monochloroacetic acid followed by soaking in aqueous 50% sodium hydroxide solution. The DS obtained by the treatments were 0.072 for the former and 0.077 for the latter. Thus it was possible to compare the properties of the products of the two widely different preparations at approximately equal substitutions. Results of the tests are shown in Table III. In general, the properties of the sample carboxymethylated by the aqueous alkali method were superior to those of the sample prepared by the nonaqueous method. This superiority was partially due to the shrinkage (about 33% in area) and resulting increase in weight of the fabric because of treatment with 50% alkali. The strength and flex abrasion resistance of the sample of the nonaqueous method was decreased significantly from the original values of the untreated cloth. The hand of the nonaqueous sample was very similar to that of the untreated. Stiffness determination, as measured with the Tinius Olsen stiffness tester, indicated a bending moment of 7.2 for this sample, compared with 5.2 for the untreated one. The alkali method sample, bending moment 41.9, was much stiffer.

TABLE III. Comparison of the Properties of Cottons Carboxymethylated by the Aqueous and Nonaqueous Methods

Property	Untreated	Carboxymethylated cotton: By aqueous alkali method	Carboxymethylated cotton: By nonaqueous method
Degree of substitution	—	0.077	0.072
Thread count, W×F	49×49	60×60	52×52
Weight, oz./sq. yd.	4.8	7.5	5.3
Thickness, in.	0.0147	0.0174	0.0152
Moisture regain, %	6.6	11.5	7.8
Breaking strength, lb.	56.8	57.5	48.4
Elongation at break, %	16.0	39.7	19.7
Tearing strength, Elmendorf, lb.	4.8	6.5	2.8
Tearing strength, trapezoid, lb.	8.2	14.6	7.0
Abrasion, flex, cycles*	964	2630	245
Abrasion, flat, cycles*	69	212	207
Stiffness (bending moment), $\times 10^{-4}$ in.-lb.†	5.2	41.9	7.2

* Abrasion tests were performed with the CSI-Stoll-QM Universal Wear Tester.

† Stiffness was measured with the Tinius Olsen stiffness tester.

The two samples and the untreated were examined under the microscope for a further comparison of differences produced by the methods of preparation. Prior to yarn cross-sectioning, samples were dyed in 1% aqueous methylene blue. In Figure 2A, a photomicrograph of cotton carboxymethylated by the aqueous alkali method shows a relatively uniform reaction, with all of the fibers swollen. Variation in shades of dye appears in some of the fibers, an indication that the reaction was not completely uniform at the fiber level. Figure 2B shows the lack of uniformity and comparatively little swelling obtained on carboxymethylation by the nonaqueous method. Within the larger fibers, uneven distribution of the dye indicates uneven treatment. Figure 2C is a photomicrograph of the cross section of a yarn of the untreated fabric.

Substituted Carboxymethylated Cottons by Treatment with α-Halocarboxylic Acids

The use of other α-halocarboxylic acids for the etherification of cotton by this nonaqueous method

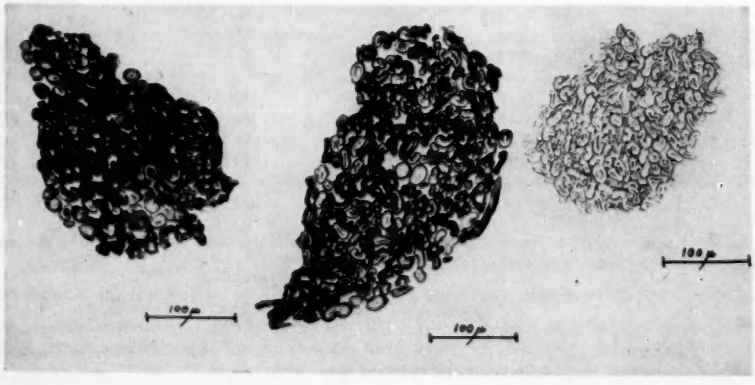

Fig. 2. Cross sections of carboxymethylated and control yarns. (*A*) relatively uniform carboxymethylation by aqueous alkali method—most fibers swollen, (*B*) nonuniform carboxymethylation by nonaqueous method—comparatively little swelling, and (*C*) untreated cotton yarn.

was investigated. Samples of the 12/5 sewing thread were mercerized, washed, and solvent exchanged from the wet state to methanol and benzene. Skeins of the activated cotton were soaked in 5% solutions of the α-halocarboxylic acid in isopropanol, excess removed, and the cotton then treated with a 12.5% methanol–87.5% isopropanol solution of enough sodium hydroxide to neutralize the acid and yield an excess concentration of 0.3%. This treatment was at reflux for one hr. Samples were then neutralized, washed with water, and extracted with isopropanol to remove reactants and byproducts. Table IV shows the α-haloacids that were used and the products that were obtained. Using the fixed conditions, the substitutions were low. No attempts were made to vary conditions to achieve higher DS, but it is believed that fibrous α-alkylcarboxymethylated cottons of DS comparable to those obtained with monochloroacetic could be achieved.

Summary and Conclusions

Cotton fiber, thread, and fabric were carboxymethylated by a nonaqueous method which consisted of an activation pretreatment, solvent exchange to remove water, impregnation with an isopropanol solution of monochloroacetic acid, and reflux treatment with 0.3% sodium hydroxide in a mixture of methanol and isopropanol. The product had a DS less than 0.1, but this could be increased by retreatment or a mercerization pretreatment. The extent of reaction was affected by innate differences in the properties of the cotton. Good rank correlations between DS and a number of the physical properties of the untreated fiber have been shown.

At equal substitution, the textile properties of cotton carboxymethylated by the nonaqueous method and the aqueous alkali method were compared. Strength and abrasion properties of the former were inferior to those of the untreated. Photomicrographs indicated a somewhat uneven reaction.

α-Methyl-, α-ethyl-, α-propyl-, α-decyl-, and α-cetylcarboxymethylated cotton were prepared in low DS by adaptation of this nonaqueous method. The appropriate α-halocarboxylic acid was used as etherifying agent.

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TABLE IV. α-Alkylcarboxymethylated Derivatives Prepared by Nonaqueous Treatment of Cotton with α-Halocarboxylic Acids

Etherifying agent	Derivative prepared	DS
α-Chloropropionic acid	Cell-O-CH(CH_3)COOH α-methylcarboxymethylcellulose	0.048
α-Chlorobutyric acid	Cell-O-CH(CH_2CH_3)COOH α-ethylcarboxymethylcellulose	0.019
α-Bromovaleric acid	Cell-O-CH($CH_2CH_2CH_3$)COOH α-propylcarboxymethylcellulose	0.022
α-Bromolauric acid	Cell-O-CH($C_{10}H_{21}$)COOH α-decylcarboxymethylcellulose	0.017
α-Bromostearic acid	Cell-O-CH($C_{16}H_{33}$)COOH α-cetylcarboxymethylcellulose	0.019

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Electroanalysis with Controlled Cathode Potential of Metallic Copper Applied to Fabrics as Metallo-Organic Fungicides

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Abstract

A method is described for the electrolytic determination of copper in fabrics treated with organo-copper fungicides. The samples investigated contained fire retardants as metallic oxides, among which were those of antimony, calcium, zinc, and iron. Antimony offers the greatest interference in the electrolytic determination of copper. This interference was eliminated by depositing the copper from ammonium tartrate solution with careful control of the cathode potential, using a laboratory potentiometer to measure the voltage. Data are presented showing that copper may be electroplated from ammonium tartrate solutions, containing a six-fold greater concentration of antimony, with a cathode potential of -0.60 volts. Standard deviations for analysis of these solutions were small (± 0.001 mg. Cu/ml.), giving an error term of 0.05% (standard dev. of the mean, σ/mean determination $\times 100$). Results are also given for analyses of fabrics containing copper-8-quinolinolate and copper naphthenate singly or in mixture. Standard deviations computed for these analyses also were small. A rapid and safe method for digesting cloth samples with sulfuric and perchloric acids is described.

Introduction

Application of fire retardants as metallic oxides to fabrics along with copper fungicides (ranging in concentration from 0.09 to 0.5% copper by weight of the fabric) creates a problem of analysis of the copper metal in the presence of other metals. The electrolytic determination of copper in the usual manner from solutions containing dilute sulfuric acid as electrolyte is unsuitable when antimony is present. The normal potentials of copper and antimony are close enough to require more careful control of the electrolysis. The following values of these potentials are given by Latimer [5]:

$$Cu^{++} + 2e = Cu \quad E^0 = +0.337v \qquad (1)$$

$$SbO^{+} + 2H^{+} + 3e = Sb + H_2O \quad E^0 = +0.212v \qquad (2)$$

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Furman [2] separated copper and antimony by depositing copper from fluoride solution after oxidizing antimony to the pentavalent state with potassium persulfate. Presumably the effect of fluoride was to make the reduction potential of antimony more negative by forming a stable complex, thus preventing deposition of antimony. Electrolyses with these fluoride solutions necessitated the use of paraffin lined beakers and cover glasses.

For best results in the separation of copper and antimony, the use of a complexing agent can be supplemented by the technique of electrolysis with control of the cathode potential. This technique [1] consists of adjusting the applied potential of an electrolytic cell to maintain the potential of the cathode, with respect to some reference electrode, constant at some desired value. The cathode potential chosen lies at some value between the deposition potentials of the two metals to be separated. Thus Schoch and Brown [8] successfully separated copper and antimony by using an electrolyte containing hydrochloric acid and tartaric acid, and by maintaining a cathode potential of −0.50 to −0.65 volts. A somewhat more accurate procedure was worked out by Lingane [6]. It consists of using an electrolyte containing sodium tartrate and tartaric acid, and a cathode potential of −0.36 volts vs. the saturated calomel electrode.

The method which will be described for the determination of copper in fabrics treated with a fungicide is essentially that given by Lingane for metallic samples. The composition of electrolyte and conditions of electrolysis were changed slightly because of the nature of the sample studied. The cloth samples were digested with a mixture of perchloric and sulfuric acids. The insoluble calcium sulfate formed was removed by filtration. The excess acid was neutralized with ammonia and a slight excess of ammonia was added. Antimony was thus partially precipitated as the hydroxide and was removed by the filtration procedure. After adding the ammonium tartrate to the filtrate and adjusting the pH of the solution with sulfuric acid, the electrolysis was carried out at a controlled cathode potential.

A high pH favors the electrolytic separation of copper and antimony. This is shown in Equations 1 and 2. Hydrogen ion affects the potential of antimony, changing it to more negative values. Lingane chose a pH of 4.0–4.5 as the optimum value for the separation of copper from tin and antimony. Experimental investigation in this laboratory established that a pH of 5–6 was suitable for the electrolyte being discussed in the present work. At this pH, and with a concentration of 12 g. ammonium tartrate/200 ml. electrolyte, polarigraphic studies in this laboratory showed that copper is deposited at a cathode potential of −0.60 volts vs. the saturated calomel electrode without interference by antimony.

Methods

Polarigraphy of Solutions Containing Copper and Antimony

A series of polarigrams was taken for copper and antimony in electrolytes containing sulfate and various concentrations of ammonium tartrate. It was necessary to establish the deposition potentials of copper and antimony in these solutions and to determine the effect of tartrate concentrations on the deposition potentials of these metals.

The polarigrams were carried out using a Sargent XXI pen recording polarigraph with dropping mercury electrode. All solutions contained 1% gelatin and were deoxygenated with nitrogen for 15 min. before each run. The concentration of copper as copper sulfate was always 6×10^{-4} *M* and that of antimony as antimony potassium tartrate 2×10^{-3} *M*. One of the supporting electrolytes used was 10% ammonium tartrate. The remaining three electrolytes contained 30% ammonium sulfate plus 3, 6, and 9% ammonium tartrate respectively. The 30% ammonium sulfate concentration was selected because preliminary studies on digesting cloth samples with perchloric-sulfuric acid mixtures showed that this amount of sulfate was left after digestion. The pH of each solution was adjusted to between 5 and 6 with ammonium hydroxide using pHydrion paper.

Polarigrams were run for copper and copper-antimony mixtures in the four above-mentioned solutions. In all cases a reduction wave was obtained for copper having a half-wave potential of approximately −0.40 volts vs. the saturated calomel electrode. When antimony was present its reduction wave began at −0.90 volts.

These results show that the presence of ammonium sulfate has little or no effect on the reduction potentials of copper or antimony in tartrate medium. Also, the concentration of ammonium tartrate can be varied a great deal without significant change in reduction potentials. From the results obtained, a supporting electrolyte was used, containing 30% ammonium sulfate and 6% ammonium tartrate, to determine whether copper would separate from antimony

by electroplating the copper at a controlled potential of about −0.60 volts vs. the saturated calomel electrode.

Electrolysis of Solutions Containing Copper and Antimony

In order to test the controlled potential electrolytic procedure, several runs were made on model solutions containing copper and antimony (Table I). Electrolyses were carried out using an Eberbach electrolyzer equipped with a rotating gauze anode and perforated cylindrical cathode of platinum. Control of the cathode potential was performed manually by means of a circuit composed of the cathode, a calomel electrode immersed in the electrolyte, and a Beckmann Model G pH meter set to give voltage readings (Figure 1).

Stock solutions of copper sulfate and of antimony potassium tartrate were prepared. Each of these solutions contained approximately 2 mg. of the respective metal/ml. Aliquots were added to a supporting electrolyte containing either 10% ammonium tartrate or 30% ammonium sulfate and 6% ammonium tartrate, the pH being adjusted to about 5–6 in each case. The results obtained are shown in Table I.

As seen in Table I, the precision of this method, as computed in terms of standard deviation, is good. All the copper plates obtained were pink in color without any visual evidence of antimony. The remaining electrolytes were tested qualitatively with potassium ferrocyanide to determine completeness of the electroplating of the copper. Potassium ferrocyanide was experimentally established to give a positive test for copper at a concentration of 4×10^{-2} but not at 2×10^{-2} mg./ml.

The copper content of the stock solution was also determined by titration using the iodine-thiosulfate procedure [4]. Sodium thiosulfate solution was standardized with both potassium dichromate and potassium iodate, giving a value of 0.1028 *N* and 0.1029 *N*, respectively. This standard thiosulfate solution was then used to titrate the iodine liberated by oxidizing iodide with aliquots of the stock solution of copper. Four such titrations gave identical values of 2.011 mg. copper/ml. These are lower than the average value of 2.032 mg. obtained with the electrolytic procedure. No reason can be given

TABLE I. Results for Determination of Copper in Solutions Containing Antimony, Using Tartrate and Sulfate as Supporting Electrolytes

Run no.	Supporting electrolyte	Ml. stock Cu* sol'n added	Ml. stock Sb† sol'n added	Found, mg. Cu	Found, mg. Cu/ml.
1	10% ammonium tartrate	5	30	10.16	2.032
2	10% ammonium tartrate	10	—	20.34	2.034
3	30% ammonium sulfate, 6% ammonium tartrate	5	10	10.18	2.036
4	30% ammonium sulfate, 6% ammonium tartrate	5	30	10.16	2.032
5	30% ammonium sulfate, 6% ammonium tartrate	10	50	20.32	2.032
6	30% ammonium sulfate, 6% ammonium tartrate	20	—	40.54	2.027
Average mg. Cu/ml.					2.032
Standard deviation of the mean (mg./ml.)					±.001

* 2 mg. Cu as copper sulfate/ml.
† 2 mg. Sb as antimony potassium tartrate/ml.

at this time for this apparent discrepancy. However, the electrolytic results were considered to be sufficiently reliable to test the method using cloth samples.

Analysis of Fabric Treated With Copper-8-Quinolinolate

The fabrics taken for study were 12.29-oz. cotton duck treated with copper-8-quinolinolate, copper naphthenate, a mixture of these two fungicides, water repellents, and fire retardants. A large enough sample (5 g.) was used to assure reasonable accuracy when the copper content was low. Copper deposited on the cathode was weighed on a semi-micro balance.

Several methods were tried for acid-digesting fabric samples. These included various ways of heating with mixtures of sulfuric and perchloric acids, in some cases with the aid of nitric acid. Ashing of samples was found to be inadequate because fusions occurred which significantly affected the copper determinations. The best method found was that described by Kahane [3] for the digestion of animal tissues. The adaptation by this laboratory of Kahane's method involved heating of the sample with sulfuric acid until the most easily oxidized materials in the fabric have been destroyed. Perchloric acid was then added dropwise, with continued heating, at such a rate that it was consumed as fast as it was added. This digestion is rapid and safe.

The digest was a colorless or slightly yellow liquid containing a white or gray residue. Upon dilution, treatment with ammonium hydroxide, and filtering, calcium sulfate was removed along with any iron (as hydroxide) and part of the antimony (as hydroxide). The filtrate containing the copper was then treated with ammonium tartrate, the pH adjusted, and electrolyzed.

An Eberbach electrolyzer was used for plating out the copper. The cathode potential was measured by means of a circuit composed of the cathode connected to the glass electrode terminal of a Beckmann model G pH meter and a saturated calomel electrode dipped into the electrolyzing solution and connected to the saturated calomel electrode-terminal of the pH meter. The pH meter was set to read potential. The cathode potential was kept constant at −0.6 volts vs. the saturated calomel electrode by manually adjusting the voltage across the electrolytic cell. A schematic diagram of the apparatus is shown in Figure 1.

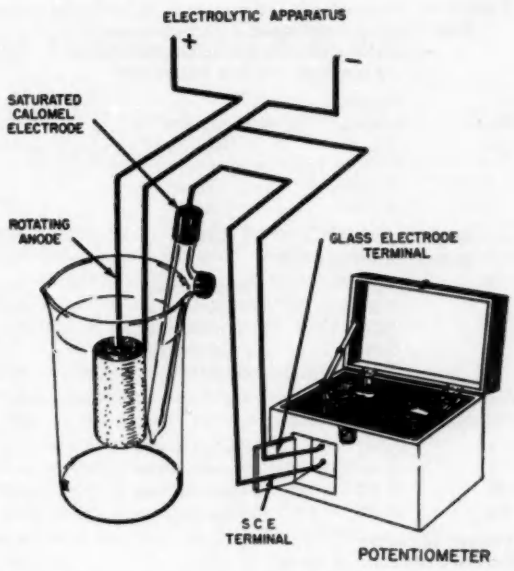

Fig. 1. Diagram of potentiometer-electroanalyzer circuit for the manual control of cathode potential.

Procedure

Weigh out a 5 g. sample, cut into ¼ in. squares, and place in a 300 ml. Erlenmeyer flask. Add 35 ml. concentrated sulfuric acid. Place a glass V, made from a 4 ml. glass rod, over the lip of the flask as support for a small short stemmed funnel, making sure that the stem touches the side of the flask. Heat the flask and contents to brisk reaction over a Meker burner in a hood provided with a safety shield. After about 45 min. start adding 72% perchloric acid dropwise, with continued heating, at such a rate (about 3 drops/min.) that the vigorous reaction continues. Oxidation should be complete in 30–40 min. after the addition of about 4 ml. perchloric acid. At this point remove the funnel and continue heating for an additional 30 min. to remove all traces of chlorine.

Cool and dilute (carefully!)[2] with 50 ml. of water. Make the solution slightly alkaline to litmus by dropwise addition of ammonia. Filter through No. 40 Whatman filter paper. Dilute the filtrate to approximately 200 ml. Add 12 g. ammonium tartrate and adjust the pH to between 5 and 6 with sulfuric acid.

[2] Perchloric acid is a powerful oxidizing agent. Addition of water to a hot organic digest containing concentrated perchloric acid could result in an explosion. Cooling of the digest is imperative to minimize this hazard.

TABLE II. Determination of Copper in 12.29-Ounce Cotton Duck Treated with Copper Naphthenate and Copper-8-Quinolinolate, in Combination with Water Repellents and Fire Retardants

Run no.	Sample weight, g.	Cu applied to fabric as	% Cu found
1	5.163	none	.007
2	5.176	none	.001
Average % copper			.004
Standard deviation of mean			.003
3	5.038	Naphthenate	.346
4	5.075	Naphthenate	.335
5	5.024	Naphthenate	.354
6	5.045	Naphthenate	.352
7	5.037	Naphthenate	.347
Average % copper			.347
Standard deviation of mean			.003
8	5.247	8-Quinolinolate	.059
9	5.047	8-Quinolinolate	.060
10	5.095	8-Quinolinolate	.080
11	5.025	8-Quinolinolate	.065
Average % copper			.066
Standard deviation of mean			.005
12	5.425	Naphthenate and 8-Quinolinolate	.373
13	5.249	Naphthenate and 8-Quinolinolate	.388
14	5.215	Naphthenate and 8-Quinolinolate	.374
15	5.183	Naphthenate and 8-Quinolinolate	.376
Average % copper			.378
Standard deviation of mean			.003

Carry out the electrolysis using the arrangement shown in Figure 1. Slowly increase the applied potential until the cathode potential reaches −0.6 volts vs. the saturated calomel electrode. During the electrolysis the cathode potential will tend to change; frequent manual adjustments of the applied potential will be required. After an hour, test the electrolyte for copper by removing 2 ml. of solution and treating with 5% potassium ferrocyanide solution. If a pink color is obtained, continue the electrolysis. When no test is obtained for copper in the electrolyte, remove the cathode, rinse successively with distilled water and 95% ethyl alcohol. Dry the cathode at 105° C. for a few minutes. Cool and weigh.

Results

Table II gives results obtained with fabrics containing copper as the naphthenate and 8-quinolinolate. All of the deposits were bright pink in color. The results are reproducible with relatively small standard deviations. Since the actual copper content of the fabrics was not known, no analysis of the quantitative data can be given for the accuracy of these determinations. However, from the precision obtained in these runs and the fact that all the copper is known to have been deposited, this method affords reproducible determinations.

Using the manual control procedure as presented for adjusting the potential, there is some chance that the cathode potential may rise above −0.6 volts, causing antimony to deposit as a black plate. Whenever this occurred the electrolytic circuit was merely broken for about 10 min. The antimony then redissolved and the electrolysis was continued. The use of an automatic potentiostat [6] would eliminate this difficulty.

The time of electrolysis is usually about 3 hr. However, as many as four electrolyses have been run simultaneously by connecting the saturated calomel electrodes to the common terminal of the pH meter and switching in the desired cathode, whose potential is to be read. In this way the time required per run in doing several analyses can be shortened greatly.

Summary

The method of electroanalysis by control of the cathode potential has been applied successfully to the determination of copper in fabrics. No interference has been encountered with antimony or iron. Control of the cathode potential was carried out manually with the use of a Beckmann model G pH meter connected with a commercial electrolyzer.

Preparation of a sample of fabric for electroanalysis was easily and safely done using sulfuric and perchloric acids as oxidizing agents. This was accomplished by oxidizing a large part of the sample with sulfuric acid alone, then completing the digestion by dropwise addition of perchloric acid to the hot solution.

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The Theory of Dyeing Cellulosic Fibers[1]

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Abstract

The theory of dyeing was developed in the last 25 years, rather lately compared with the history of the synthetic dye industry. This delay was, to a certain extent, unavoidable, since sufficient knowledge of the submicroscopic structure of fibers and of the nature of aqueous dye solutions was not previously available. More recent developments of the theory are characterized by refinements in details and by its application to specific problems.

A complete theory of substantivity has still to await the elucidation of molecular attraction forces by chemical physics, but this does not hinder the basic understanding of the dyeing phenomena. As a main achievement of the theory, mass action laws are formulated which explain and describe the equilibrium of dye absorption. Since the cellulose dyes are ionized and absorbed as ions, cellulose dyeing from the standpoint of absorption equilibrium is more complex than the dyeing of acetate and synthetic fibers with non-ionic disperse dyes. This fact fully explains the tremendous effect of salt observed in direct dyeing of cellulose. It also defines the place of cellulose dyeing in the general framework of a unitary theory of dyeing.

The kinetics of dyeing is based on the concept that the rate-determining process in dyeing is the diffusion of the dye from the surface of the fiber into its interior. It can be considered as the second main achievement of the theory that it gives a satisfactory description and explanation of the rate of dyeing.

The third achievement of the theory of dyeing is the explanation of the transformations of the dye in the fiber. This was studied by X-ray diffraction and light absorption measurements. The results indicate that soluble dyes and dye-formers are absorbed in monomolecular form by the fiber, but after they are insolubilized, they exhibit in many cases a tendency to crystallize. This explains the behavior of azoic and vat dyes on aftertreatment.

The theory provides the dyer with an understanding of his everyday problems, and enables him to supplant empirical craft by scientifically controlled methods. This will be accelerated as the validity of the theory is generally recognized and accepted as a basis for teaching and learning the technology of textile dyeing.

Introduction

The century which has elapsed since Perkin's discovery of mauvein has witnessed an uninterrupted, steady progress in the synthesis of textile dyes. Many hundreds of chemists, among them leading figures of organic chemistry, contributed to this progress, and the many thousands of synthetic dyes known and used today represent the greatest cumulative effort of industrial chemistry. For every one of the commercially used dyes there were scores of others synthesized in the laboratory which were never accepted for production. Testing laboratories of the large dye manufacturers have been busy for the last 90 years with separating the wheat from the chaff in the steady stream of experimental products flowing from the synthetic departments.

The history of the development of the theory of dyeing, particularly of cellulose dyeing, is a very different one. This theory was developed only during the last 25 years, and essentially by a handful of research workers. Synthesis of dyes and theory of dyeing represent, of course, widely different targets for scientific research. The theory of dyeing is concerned with the relationships which regulate the uptake of dye molecules by fibers. The knowledge of these relationships should not only satisfy intellectual curiosity but should make possible the scientific

[1] This paper was presented at the Perkin Centennial, Symposium on Theories of Dyeing, September 15, 1956, at the Waldorf Astoria, New York.

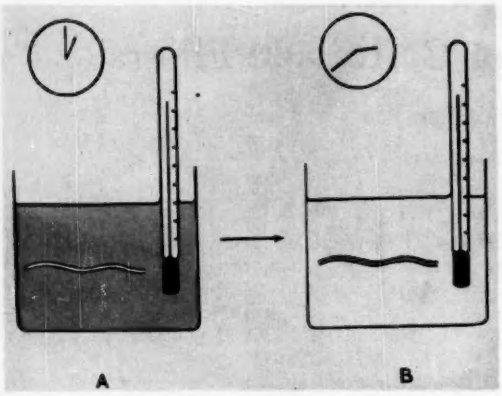

Fig. 1. Schematic illustration of the dyeing process. (A) fiber placed in a dye bath, (B) the fiber extracted the dye from the bath.

control of the dyeing process and the development of new and improved dyeing methods.

Since the theory of dyeing had not been evolved until some 25 years ago, the technique of dyeing remained, at least until that time, a merely empirical art. Why did such a long delay occur in the development of the theory?

To some extent the delay was unavoidable. The theory requires knowledge of both the structure and molecular organization of fibers and the nature of aqueous dye solutions. The fundamentals of such knowledge became available only some 25 years ago.

Stripped of all nonessentials, the basic phenomenon of dyeing is what is observed when dye solution and fiber are brought into mutual contact; the dye leaves the solution and, more or less completely, migrates into the fiber (Figure 1). It is obvious that if it is not known how the fiber molecules are built and organized, and not known whether the dye is dissolved or only dispersed in the dye bath, it is not possible to explain what is happening when fiber and dye solution are brought into contact with each other.

Why the dyeing phenomenon occurs—why the dye migrates from the bath into the fiber—is the first question the theory of dyeing has to answer, but it is not the only one. It also has to give the scientific explanation for the effect of three most important variables of the dyeing process: time, temperature, and concentration.

The textile dyer, in everyday work, has to determine how long he should leave the goods in the dye bath, whether the temperature should be raised or lowered, and, of course, how much of the dye or salt should be added to the dye bath. Where the practical dyer is asking how, the scientist is asking why, but they deal with the same three variables—time, temperature, and concentration.

Again, without knowledge of how the fiber and the dye solution are constituted, any effort to account for the effect of these variables would be futile. Therefore, it is not surprising that physical chemistry of dyeing as a science is a comparatively young one [25, 26, 27].

Molecular Attraction

Why does the dye leave the bath and why is the dye extracted, more or less completely, by the fiber? The answer, in its most general form, should be obvious: the molecules of the fiber substance attract the dye molecules. Less obvious is the answer to the next question: what are these forces of attraction?

As is known, all the solids and liquids of our world are formed by the forces of molecular attraction. Without these forces, due to the kinetic energy of the molecules, they would evaporate. Only the forces of attraction between the molecules cause gases to condense to liquids, and liquids to crystallize. Differences of the attraction forces cause crystals to go into solution in one solvent but to separate from another solvent.

Physical chemists and chemical physicists are trying to explain these forces. Nevertheless, our knowledge of them is limited. In general terms, these forces are called van der Waals forces. Specifically, they have been recognized as interaction between permanent and induced dipoles (Debye forces), as dispersion forces (London forces), and as hydrogen bonding.

Which one of these forces is responsible for the affinity of the direct dyes for the cellulose molecules —for their substantivity? As with other cases of molecular condensation phenomena, all of these forces contribute to substantivity [25, 26].

It is necessary to emphasize that it was clearly recognized 20 years ago that all kinds of attraction forces contribute to substantivity. Nevertheless, hardly a few months go by without an article pointing to one kind of attraction as responsible to the exclusion of the others, creating the impression that the theory of dyeing is in a very unsettled condition. In fact, the theory in its present form gives a satis-

factory explanation of the basic phenomenon of dyeing, although it is far from being complete.

The incompleteness lies in the lack of satisfactory explanation for the highly specific requirements for substantivity. One of these, apparently, is the presence of an uninterrupted chain of conjugated double bonds (alternating single and double C—C bonds) in the molecule. Another is co-planarity, i.e., the centers of the carbon atoms should lie in the same plane (Figure 2*a*, 2*b*). Following the recognition of the significance of the hydrogen bond for the attractive forces between dye molecule and cellulose [25], it was suggested that the substantive dye molecules must exhibit the presence of a pair of hydrogen bonding groups at a distance of 10.3 Å to correspond with the distance between the primary hydroxyl groups along the cellulose chain [17]. However, it was later demonstrated by the use of molecular models that the cellulose molecule has so many hydrogen bonding groups, namely oxygen atoms, that if a dye molecule is placed upon it, whatever the distance of the hydrogen bonding groups might be in the dye, they are close enough to oxygen atoms of the cellulose to form hydrogen bonds [19]. This fact logically eliminates the significance of the distance 10.3 Å as evidence for, as well as against, the role of the hydrogen bond in dyeing.

Increasing the molecular weight of the dye seems to increase the affinity. The contribution of this factor is twofold: it increases the magnitude of dispersion forces between cellulose and dye and increases the tendency of the dye molecules to escape the water. This last effect can be more correctly described as an increased tendency of the water to squeeze out the dye molecules from the dye bath [7]. Actually, it represents a negative contribution of the hydrogen bonds: the dye molecule, when dissolved in water, prevents some water molecules from forming hydrogen bonds with each other; therefore, the water molecules tend to squeeze out the dye molecule. Molecular size, however, cannot be the most important structural element in substantivity, since it cannot account for the obviously higher degree of specificity observed. It is more likely that the detailed structure of the electronic cloud which surrounds the conjugated chain of the dye molecule plays an important part in the interaction between cellulose and dye, either by dispersion forces or by hydrogen bonding.

At this point, it should be remembered that the physical chemistry of dyeing is an applied science and it is not its task to establish new fundamental laws. Clearly, we cannot progress in knowledge of the affinity of dyes until we learn more about the nature of van der Waals forces. Schwalbe in his review of the theory of dyeing, written 45 years ago, quoted von Prager, who said in 1901, "Chemistry is not sufficiently developed to explain the phenomena of dyeing. For that purpose, we must study the physics of molecular forces. These are related, no doubt, to chemical constitution, but are too little known today to define the laws governing the theory of dyeing." Since that time, great progress has been made, but von Prager's statement still holds.

Admittedly, experimental material on which to base the establishment of the relationship between chemical structure and affinity of dyes is still very limited. However, before we possess the final answers to such questions as why sugar is soluble in water and silver chloride is not, questions which likewise deal with the nature of molecular attraction,

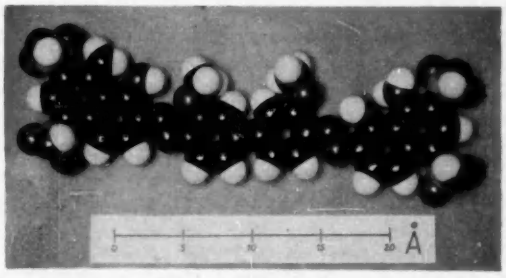

Fig. 2a. Molecular model of Chicago Blue FF built to scale. Viewed perpendicularly to the plane of the molecule.

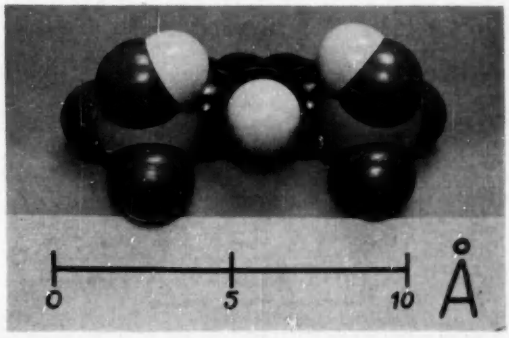

Fig. 2b. Viewed in the plane of the molecule in the direction of its longer axis.

we have no reason to think that the theory of substantivity is in a particularly backward position.

The Mass Action Law of Dyeing

In considering the three variables—time, temperature, and concentration—it is surprising to observe that no reliable experimental material dates back earlier than 1933. This appears strange in view of the tremendous quantities of dyes applied to textile materials during the previous 75 years and the immense experience gathered over that period. Unfortunately, since the industry was primarily interested in production and not in correlation of variables, practically all observations reflected the simultaneous variation of several variables, and therefore were unsuited to form the basis for a theoretical approach.

In 1933, Neale and coworkers in Manchester [16], as well as Boulton, Morton, and coworkers [5] in the research laboratories of Courtaulds in England, began systematic experiments in which the three variables were varied one by one. Their observations, but no earlier ones, can be used for discussing the physical chemistry of dyeing in quantitative terms.

One might mention a few of the pitfalls which these workers avoided but their predecessors generally did not. They used purified dye, not the commercial ones containing salt. Therefore, they could vary salt and dye concentrations independently. They varied the time of dyeing from zero to infinite; that is, from beginning until equilibrium was

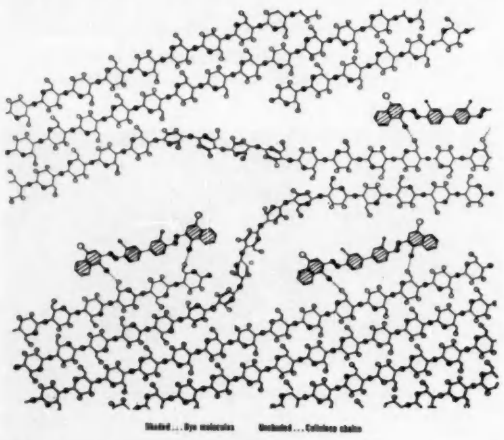

Fig. 3. Schematic illustration of the sorption of direct dyes by cellulose in the pores of the fiber. Shaded: dye molecules, unshaded: cellulose chains. Boulton [3].

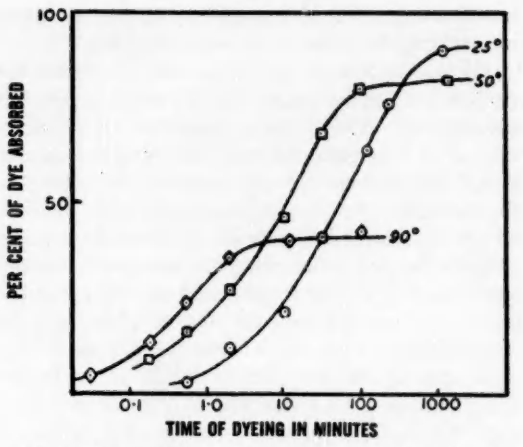

Fig. 4. Exhaustion of a direct dye by rayon as a function of time and temperature. Boulton, Morton, and coworkers [5].

reached. Therefore, it definitely could be established that the amount of dye taken up at equilibrium decreased with increasing temperature in all cases, without any exception. This was the first time it was proven that dyeing is an exothermic process.

Up to that time, it was sometimes reported that the uptake of dye increased with the temperature. Usually the observer did not wait until equilibrium was established, and often mistook the faster rate of dyeing for increased equilibrium uptake.

Figure 4 presents the classical observation of Boulton, Morton, and coworkers on the rate of take-up of a direct dye by viscose rayon. For short observation periods it can be noticed that in the experiment carried out at higher temperature, less dye is taken up by the fiber than in the experiment carried out at lower temperature. Obviously, the rate by which the dye is absorbed by the fiber is slower at lower temperature. Therefore, the state of distribution of the dye between bath and fiber is, at lower temperature, further apart from the state of equilibrium than at higher temperature. When the experiment is run long enough, equilibrium, as shown by a flattening of the absorption curve, is finally reached; it becomes clear that at higher temperature less dye is extracted by the fiber.

Rate and equilibrium of dyeing are much too often confused in practice, probably because the practical dyer is interested in the exhaustion of the dye in a limited time. It is, however, regrettable when the theory of modern carrier dyeing and high tempera-

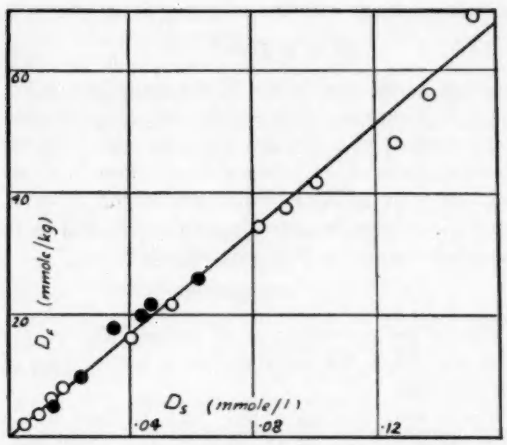

Fig. 5. Adsorption and desorption of *p*-nitro-aniline N-bis 2-hydroxy ethyl aniline by acetate. Arches: adsorption, dots: desorption. Bird, Manchester, and Harris [2].

ture dyeing of hydrophobic fibers is blurred by lack of distinction between rate and equilibrium. High dyeing temperature and, in most cases, the addition of carriers serve not to increase the affinity of the dye as measured by the equilibrium absorption but to increase the rate of absorption.

Let us consider the relationship to be expected between the dye concentration in the bath and the amount of dye on the fiber.

The effect of dye concentration on dyeing is, of course, qualitatively obvious—more dye in the bath, more dye on the fiber. Quantitatively, the simplest relationship presents the concentration of the dye on the fiber as proportional to the concentration in the dye bath. Experimentally, such a linear relationship has been observed with non-ionized dyes.

Non-ionized dyes are insoluble in water; therefore only the disperse dyes belong to this group. They are used in the dyeing of acetate, triacetate, nylon, and polyester fibers, but not cellulose. In careful experiments where the equilibrium conditions were definitely established, this linear relation [2] was observed for acetate (Figure 5) by Bird and coworkers, and for polyethylene terephthalate by Schuler and Remington [20]. The quantitative formulation of such an equation is

$$D_f = K \times D_s$$

where D_f is the concentration of the dye in the fiber, D_s is the concentration of the dye in the solution, and K is the partition coefficient.

More complex are the relations where the dye is ionized, such as with the direct dyes and cellulosic fibers.

The tremendous effect of salt on dyeing had been noticed immediately after the discovery of the first synthetic direct dyes, Congo Red and Benzopurpurine 4B. Somewhat later, Knecht observed that in the absence of salt no dyeing occurred in some cases. This started speculations on how salt addition influenced dyeing. At that time, knowledge of the submicroscopic architecture of cellulosic fibers—the structure and organization of cellulose molecules—as well as of the physical chemistry of dye solutions was lacking. Whenever real knowledge is lacking, imagination and speculation are rampant. More than lack of knowledge, the greater handicap was, as often is the case, that many of the research workers "knew"—believed they knew—something which, in fact, was not so. The colloidal nature of the dye solution loomed large in this "knowledge," and such typically colloid chemical effects as coagulation played a great role in the speculation on the salt effect in dyeing cellulose. Physical-chemical investigations showing that solutions of direct dyes behaved essentially like regular ionic solutions [25, 26, 27] paved the way to the modern theory of the salt effect.

Neale [16] was the first to collect systematic data on the salt effect, by keeping all other variables constant. Figure 6 shows some of his results. It will be seen that the uptake of the dye in these examples increases five- and tenfold by increasing the concen-

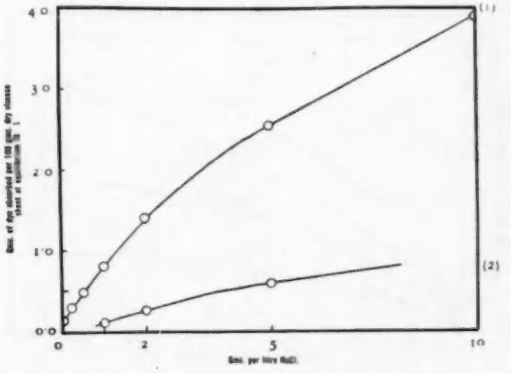

Fig. 6. Variation of the absorption at equilibrium of Benzopurpurine 4B and Chicago Blue FF with concentration of salt. Dye, 0.05 g./lb. (1) Benzopurpurine 4B, (2) Chicago Blue FF. Neale and coworkers [16].

tration of salt in the dye bath from 0–1–2%. How is that effect to be explained?

The answer is a very simple one. Because of electroneutrality, the fiber cannot absorb the dye anions without absorbing an equivalent quantity of gegenions (counterions, i.e., ions compensating the charge of the dye ion) such as sodium ions. Obviously, the gegenions become part of the equilibrium. If more gegenions are present in the solution, they are more easily absorbed by the fiber. To increase the concentration of the gegenions in the solution, it is necessary to add salt.

It is not too difficult to derive a general mass law of the equilibrium state of the uptake of an ionized dye by the fiber, expressing the dependence of the amount of dye in the fiber on the concentration of the dye-ion and the other ions in the dye bath [26, 29].

It is assumed that the dye to be distributed between the two phases, fiber and solution, is the sodium salt of an n-valent dye anion. The dye anion possesses affinity for the fiber, but cannot accumulate in the fiber without taking along the equivalent amount of sodium ions. Let us assume that the number of sites available for the dye in the fiber is unlimited; that is, it is large in relation to the number of sites actually occupied. As soon as an infinitely small number of dye anions are taken up by the fiber, it acquires a negative electrostatic potential. The electrostatic forces due to this potential repel dye anions but attract sodium ions. In equilibrium, electrostatic and specific affinity forces balance each other, and the partition of the dye ion will be in accordance with the following equation:

$$D_f = K\, D_s e^{-nFX/RT} \qquad (1)$$

where K is the free energy of absorption of the dye ion, n is its valency, F is one faraday, X is the electric potential, R is the gas constant, and T is the absolute temperature. Since the sodium ions are assumed to be without specific affinity for the fiber, their distribution between the two phases will be in accordance with the following equation:

$$\mathrm{Na}_f = \mathrm{Na}_s e^{FX/RT} \qquad (2)$$

Na_f is the concentration of sodium ions in the fiber and Na_s is the concentration of sodium ions in the solutions.

These equations go a long way to explain the equilibrium uptake of an ionized dye. However, they contain two quantities which are difficult to determine experimentally—X and Na_f. The task is simplified if we assume that the fiber does not contain other anions besides the dye ions. In this case, because of the law of electroneutrality,

$$\mathrm{Na}_f = n\, D_f \qquad (3)$$

Combination of the three equations yields

$$D_f = K\, D_s^{1/(n+1)} \times \mathrm{Na}_s^{n/(n+1)} \qquad (4)$$

This clear and almost obvious relationship dispels all the mystery which previously has surrounded the salt effect. It can be called the mass action law of direct dyeing. It expresses in quantitative terms the fact that the equilibrium exhaustion of an ionized dye does not depend on the concentration of the dye alone in the bath but also on the concentration of all other ions. The mode of action of Glanber's salt or common salt added to the dye bath for the purpose of increasing absorption of the dye is not a reduction of the solubility of the dye, nor an increase of the particle size of the dye, nor coagulation of the dye, as it was frequently assumed. The mode of action of the salt added is rather facilitation of the compensation of the electrostatic charges imparted to the fiber by the absorbed dye ions.

Equation 4 does not contain the electric potential, but only variables which are easily determined by experiments and a constant, K, representing the affinity of the dye ions to the fiber.

It is interesting to note that, according to the equation, the salt effect is stronger when the dye ion has a higher electrovalency. The absorption of a disulfonic dye acid is more sensitive to addition

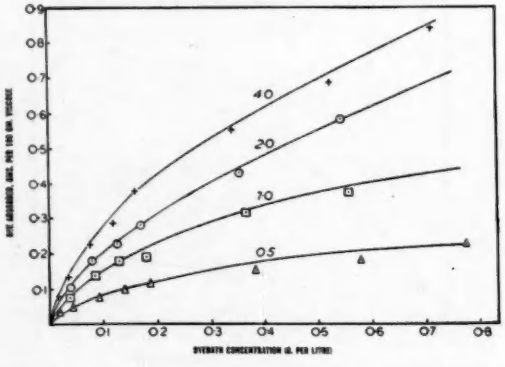

Fig. 7. Absorption isotherm of Chrysophenine at 97.5° C. on cellulose film. Na_2SO_4 concentration in g./l. indicated on each curve. Willis, Warwicker, Standing, and Urquhart [29].

of salt than that of a monosulfonic dye acid; absorption of tri- and tetrasulfonic acids (common among direct dyes) is even more sensitive.

The quantitative expression derived for the salt effect has been confirmed by experiments carried out in 1945 at the British Cotton Research Association [29].

Figure 7 shows the degree of absorption of dye with increasing concentration of the dye in the solution, each curve representing a constant concentration of sodium sulfate present in the bath.

At fixed salt concentration there should be a linear relationship between the logarithm of the dye concentration and the logarithm of the amount of absorbed dye. Figure 8 shows that this is the case. On the other hand, at fixed dye concentration there should be a linear relationship between the logarithm of the salt concentration and the logarithm of the concentration of absorbed dye. This requirement is also fulfilled.

As a final proof of this equation it is required that if the ratio of the salt to the dye is kept constant, a linear relationship exists between the dye concentration in the bath and in the fiber. Figure 9 shows that this requirement is also fulfilled by the experiments, with truly amazing exactness.

Equation 4 gives a clear and simple description of the salt effect, but the assumptions on which it is based represent, no doubt, simplifications of actual conditions. The assumption that the total sodium ion concentration inside the fiber is due to the counterions alone is open to criticism. It would mean that the salt itself is not present in appreciable amount in the fiber. This is certainly not true for high concentrations of salt.

Experimentally, the slopes of these graphs are definitely different from the calculated slopes. Several reasons are possible: the dye might be more or less associated to aggregates in the solution, or it might be incompletely ionized. It might also be due to the fact that the amount of salt inside the fibers was not negligible. Alternative assumptions might lead to better agreement. The main refinement proposed is that the distribution of salt between fiber and bath follows the Donnan principle; consequently, at high salt concentration the amount of salt inside the fiber becomes appreciable [16, 27].

The equilibrium constant, K, represents the free energy of the dyeing process, or the affinity of the dye. What values of affinity we derive from the experimental data depend on what assumptions we make as to the available volume in the fiber and distribution of salt between the two phases.

Affinity values have been calculated for a few dyes. They were between 3000 and 6000 calories per mole of dye. Since the equilibrium changes exponentially with the free energy, this means ratios in the equilibrium position of about $\times 10$. These are precisely the data which we need (in greater quantity) to establish the correlation between substantivity and chemical constitution.

Unitary Theory of Dyeing

Before discussing the absorption of direct dyes by cellulose, we briefly mentioned the simpler relation-

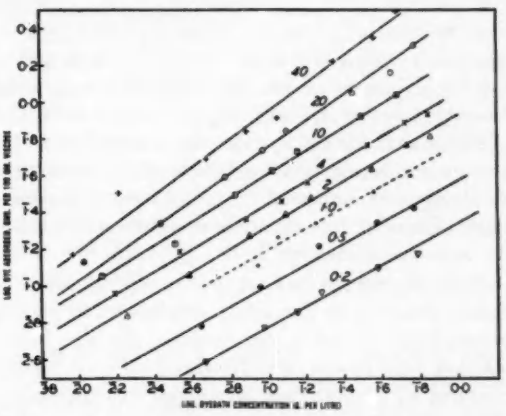

Fig. 8. Absorption isotherms of Chrysophenine on cellulose film at 97.5° C. Concentration of NaCl in g./l. is indicated on each line. Willis, Warwicker, Standing, and Urquhart [29].

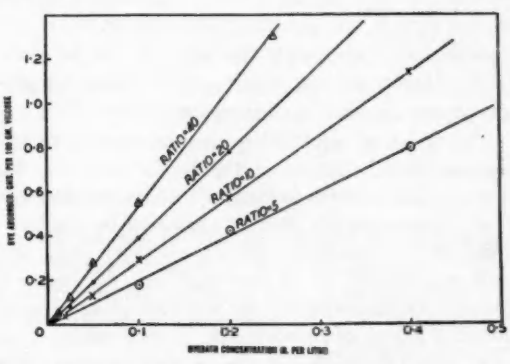

Fig. 9. Absorption isotherm of Chrysophenine at 80° C. on cellulose film for fixed salt/dye ratios. Willis, Warwicker, Standing, and Urquhart [29].

ship which prevails with non-ionized dyes. There is a third important case of dye absorption, which comprises the uptake of ionized dyes by such fibers which contain mobile exchangeable ions of the same sign (usually negative) as the dye ion. The best known example is the so-called acid dyeing of wool. When wool is treated with an acid such as sulfuric acid or acetic acid, the keratin molecule combines with hydrogen ions and the fiber takes up at the same time the equivalent amount of sulfate or acetate ion. Such a wool fiber acts now as an ion exchange body. When an anionic dye is added to the dye bath, the colored anion penetrates the fiber and more or less completely displaces the colorless sulfate or acetate ion. Because the process is that of exchange of equivalent amount of ions, the electroneutrality is not disturbed. The equilibrium absorption isotherm has the form of a straight proportionality between the concentration of the dye ions in the bath and in the fiber, just as is the case with non-ionic dyes. Usually, however, the exchangeable ions, that is, the available sites for the dye ion, do not represent such a large excess; in this case the equilibrium follows the Langmuir isotherm. This isotherm is the mass action law of the dissociation equilibrium applied to the adsorption phenomena.

It states that the ratio of the concentration of the dye in the fiber to the available unoccupied sites is proportional to the concentration of the dye in the solution. Of course, this relation has to be further modified if, for instance, available sites of various affinity are present.

In order to replace effectively the colorless anion, the dye anion has to possess higher affinity for the protein fiber. It appears, however, that the affinity of the dye anion for the protein molecule is not quite as specific as that of the direct dye for cellulose. It was shown that the affinity of the anion for protein increases with the molecular weight [21].

This type of equilibrium is not limited to the protein fibers. Dyeing of the acrylic fibers by the cuprous ion method follows the same relationship. The polyacrylonitrile fiber is converted by combination with cuprous ions to an ion exchange body, and becomes capable of undergoing the dye process through replacement of the colorless ions (introduced as anions of cuprous salt) by dye anions.

In this discussion of the dyeing process with anionic dyes, it was assumed that the fiber is brought into contact with the dye after the fiber was converted into the ion exchange body. However, this mechanism is valid even in those cases where the dye and mineral acid are applied simultaneously to a protein fiber. The hydrogen ion and the colorless small anion diffuse rapidly in the fiber before the large dye ion can enter it to any measurable extent. On the other hand, the take-up of the acid (hydrogen ion and its colorless gegenion) by the fiber represents a true ionic absorption, and it obeys the same mass action law as the take-up of an ionic dye by a non-ionic fiber (for example, in the direct dyeing of cellulose). In the reaction of protein fiber with an acid the hydrogen plays the same role as dye ion plays in the dyeing of cellulose.

In summarizing the equilibrium conditions of dyeing, we distinguish between three types.

The first is the take-up of a non-ionic dye by a non-ionic fiber. For this case the rule of the constant partition coefficient holds. The application of disperse dyes to acetate, triacetate, polyester, polyamide, and polyacrylonitrile falls into this category.

The second is the ion exchange mechanism, where the distribution of the dye ion between the two phases follows the Langmuir isotherm. This is the mechanism of dyeing of protein and polyamide fibers with acid dyes, as well as dyeing of polyacrylate nitrile fibers by the cuprous ion method.

The third mechanism is that of ionic absorption, characterized by the dependence of the equilibrium on the salt concentration. Dyeing cotton and rayon by direct dyes is the most important example for this mechanism.

At the end of the nineteenth century several theories of dyeing were proposed. One theory was characterized as the theory of solid solution, another as a theory of adsorption, and a third as the theory of salt formation. At that time, each claimed general validity. Since the end of the 1920's, it became customary to divide the validity of these theories among the various fibers. It was frequently maintained that salt formation holds for the protein fibers (wool and silk); adsorption holds for the cellulosic fibers (cotton and rayon) and the theory of solid solution holds for acetate. Later, man-made protein fibers were added to those which follow the theory of salt formation; nylon, Dacron,[1] and Orlon[1] to those which follow the theory of solid solution, at least as far as dyeing with disperse dyes is concerned.

[1] Du Pont trademark.

This division of the theory of dyeing had some merits, as it helped to bring a semblance of order into a multitude of phenomena. However, now the time has come to dispense with it in favor of a unitary concept of the theory of dyeing. In the unitary approach, a theory of dyeing is formulated on a common basis for all fibers, and the peculiarities of individual kinds of fibers (as well as the peculiarities of individual kinds of dyes) are accounted for by variations of definite parameters.

From the standpoint of the dependence of distribution of dye between fiber and bath, the state of ionization of dye and the number and nature of absorptive sites in the fiber are the determining factors. The basic mechanism of dye absorption remains the same; its cause is ascribed to mutual molecular attraction of fiber molecules and dye molecules.

Kinetics of Dyeing

Until now time as a variable was eliminated; only the equilibrium of dyeing was discussed. Now time will be considered as a variable; the rate, that is, the kinetics of the dyeing process will be outlined. It is interesting to note that the scientific study of the kinetics of cellulose dyeing started with the experiments of Neale [16], using Cellophane as a model substance instead of fiber. The observed quantities in these experiments are the concentration of the dye and the salt in the dye bath and the amount of dye in the cellulose. The first two can be kept constant by using a high bath-to-fiber ratio; this was done by Neale. The observed change with the time is, then, the increasing amount of dye absorbed by the cellulose. This is determined at constant temperature; one obtains a curve, ranging from zero amount of dye in the fiber at zero time to the equilibrium amount at infinite time, determined by extrapolation. Neale found that this curve can be expressed by a function of two quantities, the equilibrium absorption and a rate constant.

In applying this equation, Neale made two assumptions:

1. The surface of the cellulose is always in equilibrium with the dyebath. In other words, the rate-determining process is the diffusion of the dye from the surface into the interior of the cellulose. This is generally accepted today.

2. The diffusion coefficient of the dye is constant in the fiber. It was later found, by Neale himself, that this assumption is not fulfilled. Fortunately, it does not alter the agreement of the observed values with those calculated. However, it does change the meaning of the calculated values.

The three important facts emerging from the analysis of the results are:

1. The apparent diffusion coefficient of the dye in the cellulose is about 100 times lower than its diffusion coefficient in water. However, this ratio is not the same for every dye.

2. The apparent diffusion coefficient of the dye in the fiber increased more rapidly with the temperature than the aqueous diffusion coefficient.

3. The apparent diffusion coefficient in the fiber has a very low value in absence of salt, increases with increasing salt concentration up to a maximum, and then decreases.

The first two observations are easy to explain. The rate of diffusion must decrease if part of the dye is combined with the cellulose and prevents it from diffusing further. The apparent diffusion coefficient must increase rapidly with the temperature if it has a high activation energy. However, the maximum of the diffusion coefficient observed presents a serious problem, not yet solved satisfactorily.

Crank [6] gave the most complete quantitative theory of rate of dyeing. He made two assumptions:

1. In the cellulose, a portion of the dye is combined, and is therefore not diffusing. Only the free part diffuses. Partition between the two is regulated by the experimentally observed absorption isotherm (absorbed dye vs. concentration of salt).

This assumption explains the decrease of apparent diffusion coefficient with increasing salt concentration. It breaks down when it has to explain the increase of the diffusion coefficient observed with increasing salt concentration until the maximum is reacted. In order to explain this, Crank makes the second assumption:

2. The negative electric potential of the cellulose acts as a barrier for the dye ions.

With the aid of this assumption, Crank obtains complete agreement with the observed value. There is, however, one difficulty with Crank's theory; it contradicts the successful theory of equilibrium. This theory assumes a constant intrinsic partition coefficient between free and combined dye ions in the fiber and considers the observed exponential absorption isotherm a consequence of the electric po-

tential. It appears that Crank uses the idea of an electric barrier twice: first, it is implicit in his assumption of an exponential partition coefficient; second, it is explicit in his second assumption.

Accessibility

Among the factors determining the equilibrium and rate of dyeing are the number, distribution, and accessibility of absorptive sites in the fiber. The assumption that cellulosic fibers swollen in water are traversed by submicroscopic water-filled channels preceded the discovery that these fibers were partly crystalline. Later it was assumed that these channels are formed between the crystallites and that the dye molecules enter the interior of the fibers through these channels. The high dye absorption of the mercerized, and even higher absorption of regenerated cellulose, when compared with native cellulose, was explained by their higher swelling or by a higher extension of their channel system.

Some effort was made to find out quantitatively how the dimensions of the submicroscopic pathways in the fiber influence the dyeing phenomenon. These pathways were visualized as a system of intercommunicating channels, lined with cellulose and filled with water. The average diameter was calculated on the basis of such measurements as rate of flow of water, or rate of flow of air, through the swollen cellulose film. The dye molecule was supposed to diffuse through these channels.

Today, there is serious doubt whether or not such a concept is correct. The pathways appear to be formed by the amorphous or disorganized regions and filled by concentrated cellulose solutions or cellulose gel rather than by pure water. Progress of the dye in such a solution or gel would be very slow if the cellulose molecules would form a rigid network. It is more likely that the cellulose molecules are also capable of diffusion; the penetration of the dye is aided by the diffusion of the cellulose molecules. Due to the mutual attraction of dye and cellulose, the cellulose molecules will yield to accommodate the dye molecules. Calculation of average or minimum pore diameters would be hardly a realistic approach to the mechanism of penetration of the fibers by the dye molecules.

In its most general concept, dyeing from an aqueous solution is swelling of the fiber by a mixed solvent—water and dye. Penetration along pathways of the least organized portions of the fiber by the smaller water molecules lubricates the fiber molecules sufficiently to allow the larger dye molecules to follow.

State and Transformation of Dyes in Cellulosic Fibers

Among those aspects of the dyeing process which received but little attention (and that only in the last few years) has been the state of dye in the fibers. Measurements of light absorption and X-ray diffraction have been used to obtain information on this subject.

Light Absorption of Dyes in Cellulosic Fibers

Light absorption on or in the fiber is, of course, the most important function of the dyes, but it was seldom made the object of quantitative measurements until the advent of the modern recording spectrophotometers. Now it is done more or less routinely. The measurements usually refer to light reflection rather than transmission, and therefore are related to the concentration of the dye in a complex manner (Kubelka-Munk equation [12]). On the other hand, measurement of transmission through the colored cellulose film affords a direct comparison with the absorption spectrum of the dye in solvents. Two important relations which must be considered in the interpretation of these absorption spectra are the limited validity of Beer's law and the effect of the solvent.

Fundamental for these relations is the mechanism by which dye molecules absorb the light selectively at certain wave lengths. Absorption occurs as the state of the dye molecule is raised from the ground state to the excited state. The energy of the ground state of the dye molecule is determined by the existence of several resonating structures made possible by electron migration along the conjugated chain between polar atoms (such as nitrogen and oxygen) of the dye molecule. The diffuse electronic cloud surrounding the conjugated chain is therefore probably the most important structural factor determining the color of the dye.

Only in the gaseous state is the dye molecule an independent, isolated unit. In crystals, as well as in solutions, the dye molecule is subject to polarizing forces exerted either by the neighboring dye molecules, as in crystals, or by the solvent molecules, as in solutions. Deviation from Beer's Law occurs when the dye molecules have a tendency to form

associates with each other; the equilibrium of this association depends on the concentration. In such a case, with increasing concentration, the dye–solvent interaction is gradually replaced by dye–dye interaction; therefore, the influence of the polarizing forces exerted on the electronic cloud of the dye molecules is gradually changed. In consequence of this, the stability of the resonance structure of the molecule, hence its light absorption, is changed. There is no general rule as to the magnitude and direction of this change. There is, however, a definite indication for the fact that the influence of the interaction of dye with dye is more powerful than the interaction of dye with any of the usual solvents. Therefore, the state of association of the dye will have the dominant effect on its absorption spectrum. Dissociation of the aggregates is favored by increased temperature, decreased concentration, decreased electrolyte content, and use of a strongly solvating solvent. The influence of various solvents is due primarily to their influence on the state of association of the dye and not to their direct interaction with the dye molecule.

Typical is the case of Benzopurpurine 4B, one of the oldest of the direct cotton dyes [13]. In aqueous solution it gives an absorption maximum around 500 mμ, but with higher concentrations and addition of salt, this maximum shifts toward lower wave lengths, such as 480 mμ; on the other hand, addition of pyridine or alcohol shifts the maximum toward higher wave lengths, such as 525 mμ. Apparently these solvents tend to dissociate the dye–dye aggregates by forming solvates with the dye molecules. Some years ago on the basis of diffusion measurements it was concluded that certain non-ionic surface active agents form soluble complexes with direct dyes [24]. These surfactants contain a polyoxyethylene chain in the molecule and serve as leveling agents in dyeing cotton and rayon. More recently, it was observed that addition of these non-ionic surfactants shifts the absorption maximum of Benzopurpurine 4B in aqueous solutions toward 525 mμ [13]. The surfactant has practically the same effect on the absorption spectrum as pyridine, but it is effective at a much lower concentration. Recently, the effect of polyvinylpyrrolidone, a water soluble linear non-ionic polymer, on the absorption spectrum of direct dyes, among them Benzopurpurine 4B, was found to be essentially the same as that of the non-ionic surfactants, but a much lower concentration of the polymer was required to bring about the change [9].

Unfortunately, no data on the light absorption of the same dye when absorbed by cellulose is available. However, a closely related dye, Congo Corinth, was measured [11]. It was found that the absorption maximum of this dye on cellulose film was at 25 mμ longer wave length than in water.

Speaking broadly, and probably somewhat oversimplifying the actual relations, we might distinguish between the polymeric and monomeric spectra of the dye. Pyridine, alcohol, nonionic surfactant, polyvinyl pyrrolidine—as well as, apparently, cellulose—tend to shift the spectrum in the direction of the monomeric form.

X-ray Diffraction of Dyes in Cellulosic Fiber

Another attempt to gain information on the state of the dyes absorbed by cellulose was made some years ago by using the X-ray diffraction method [23]. Specifically, the question was whether the dye was crystallized or not. We could hope for an answer only if we had enough dye on the cellulose to give noticeable diffraction pattern. Without going into experimental details, it might be mentioned that we found conditions enabling us to incorporate approximately 50 g. of dye into 100 g. of cellulose. Commercial cellulose film was suitable for this purpose, but dyes were to be selected so that they combined high substantivity (affinity for the cellulose) with high solubility even in the presence of high salt concentration. The last condition is important to assure a high absorption of the dye. It was advantageous to use a medium high dyeing temperature, about 60° C. Too high a temperature reduces the absorption at equilibrium, and too low a temperature prolongs the dyeing period by reducing the rate of diffusion of the dye in the fiber. Actually, 10–20% dye in the fiber was found ample for our purpose.

In examining the direct dye, Sky Blue FF, we found that this dye, although readily crystallizable from aqueous solution, does not give any perceivable X-ray pattern when absorbed by the cellulose. It remains amorphous in the wet as well as in the dry fiber.

Any conclusion drawn from such observations has one important limitation. Crystallites under a certain particle size do not reveal their presence by X-ray diffraction. This critical particle size is of the order of 10^{-6} cm. (100 Å). Such a dye particle

would contain not more than about 1000 dye molecules.

Nevertheless, our observations seem to lend considerable support to the assumption that the direct dyes adsorbed by the cellulose form monomolecular layers on the adsorbing cellulose. Based on the usual estimates of the amount of amorphous portion in regenerated cellulose, it can be calculated that even in the case of 50 g. of dye taken up by 100 g. of cellulose, there is enough space around the accessible cellulose molecules to accommodate all the dye without the necessity of building up polymolecular layers.

There are two more pieces of information supporting the concept of monomolecular adsorption of direct dyes by cellulose. One is to be found in measurements of the absorption spectra of the dyes taken up by the cellulose, as discussed before. The other is the strong dichroism exhibited by dyed fibers.

It was observed many years ago that cellulosic fibers such as cotton and ramie when dyed with direct dyes exhibit the phenomena of dichroism. Dichroism is variation in the light absorption of polarized light with the axis of polarization in respect to the axis of the fiber. Later it was found that dyed cellulose film exhibits the same behavior as fibers and that the dichroism is a quantitative measure of the orientation of the cellulose molecules [14, 18]. It was shown that the dichroism exhibited is not due to dye crystals, but must be attributed to single dye molecules oriented with their long axis parallel to the cellulose molecules [15].

It is quite obvious that there is no reason why a direct dye should form large aggregates, crystalline or amorphous, after it is adsorbed by the cellulose in the form of a monolayer. Quite a different situation prevails with such dyes which are subjected to chemical changes after they are adsorbed by the cellulose. Foremost in importance among these dyes are the vats. These are adsorbed in the reduced water-soluble form of leuco salts and thereafter oxidized in the fiber to the not ionogenic, insoluble state. The oxidation is carried out in presence of water in the swollen fiber, where ample space is available to enable the monolayer of the dye to collapse and to form large aggregates. Such a collapse occurs in many cases, but not always. That is the reason why dye manufacturers instruct the dyers to subject the oxidized dyeings to a prolonged treatment with boiling soap solution in order to reach the final state of the dyeing. With indigo, it was found some time ago [1] that the aftertreatment produced dye particles which were visible under the microscope. When the X-ray diffraction method was applied to characterize the changes occurring during the aftertreatment of vat dyes, in several cases it became possible to detect crystallization where the microscopic investigation under the highest magnification showed the complete absence of particles [23]. Such is the case, for instance, with Caledon Jade Green FFB (dimethoxy dibenzanthrone). With indigo, it was observed that crystallization occurs immediately on oxidation, although growth to microscopically visible size requires the aftertreatment with boiling water (Figure 14).

Keeping in mind the influence of dye–dye interaction on the light absorption of dyes, it is not surprising to find that the aftertreatment of the vat dyeings often produces pronounced changes of the color. The extent of those changes is, in some cases, amazing (for example, with Indanthrene Brilliant Scarlet RK). Even more impressive than on the cotton or rayon fabric is the effect on cellulose film. The change in this case was accompanied by the formation of microscopic crystals, observed by X-ray diffraction as well as under the microscope.

Kornreich measured the light absorption of cellulose film dyed with Indanthrene Brilliant Scarlet RK, before and after the treatment with boiling water and detergent solutions [10]. He reported that the absorption maximum is shifted by the treatment from 480 mμ to about 520 mμ. Simultaneously, the extinction coefficient of the maximum increased more than 50%.

Why do vat dyes sometimes tend to aggregate in cellulose fibers? The adsorption of the dye in form of leuco ions by the cellulose molecule occurs by the same mechanism as that of direct dyes; a monolayer is formed by the dye. Each one of the leuco ions is attached directly to the cellulose molecule by specific attraction forces. Oxidation of the leuco compound changes this situation in two respects. First, the affinity of the dye for the cellulose is changed, probably reduced or even eliminated. Secondly, the thermodynamically stable bulk phase of the dye, in equilibrium with the adsorption layer, is no more the aqueous solution, but the dye crystal. Crystallization of the dye can take place easily in the water-swollen fiber. It need not occur in every case. The remaining affinity of the dye for the cellulose may still outbalance the forces of crystallization. This is appar-

ently the case with those dyes whose dyeings even after prolonged aftertreatment fail to exhibit the presence of visible or crystalline particles, such as with Indanthrene Blue RS (indanthrone).

It is obvious that the large microscopic particles and even the smaller submicroscopic but X-ray diffractive particles of the dye formed after the collapse of the monolayer cannot be accommodated in the pores or amorphous regions of the cellulose assumed to have an average cross-sectional radius of 30 Å. We must rather conclude that in growing, the particles force the fiber mass apart. There is nothing unusual in this concept, but it certainly makes appear futile any attempt to determine the pore size of the fibers on the basis of the dimensions of crystals deposited in the fibers.

The conclusions drawn from X-ray diffraction patterns had two weaknesses: first, they were obtained on fibers containing dye in large excess over commercially dyed fibers; and secondly, small crystals could not be detected by this method. Nevertheless, they were substantially confirmed by investigations of the changes of light absorption by vat dyed cellulose fibers on soaping. It was shown that in some cases the optical density increased by over 100%, and that the changes were similar to those produced by aging a freshly prepared colloidal dispersion of the dye (Figure 10). The dichroism of the dyed and soaped film showed a variety of behavior, but in most cases immediately after oxidation the dye was oriented with its resonating system along the fiber axis; after prolonged soaping it was oriented at right angles to the fiber axis (Figure 11). This was explained by the assumption that the dye crystallized to form needle-shaped crystals which lie alongside the fiber axis and in which the dye molecules are at right angles to the length of the crystal (Figure 12, [22]).

Similar phenomena occur with azo dyes when developed in the fiber by means of coupling of the naphthol with the diazo compound. Here again, the stability of the originally formed monolayer varies.

It is interesting to note that surfactants such as soaps and detergents greatly accelerate the development of the final state of the vat and developed azo dyes. In this process, solubilization of the insoluble dye by the micelles of the surfactants plays an important role. At first sight it might be surprising that a dispersing agent promoted aggregation. The action of soap in this case is that of a catalyst which facilitates the transfer of the dye from the smaller particles to the larger ones.

It was reported a few months ago by Weinstein and Wyman [28] that cellophane and gelatin films dyed with indigo exhibited absorption maxima at 662 mμ, that is, at the same wave length as the solid or crystalline dye. In solutions of organic solvents the maximum lies close to 600 mμ (Figure 13). It was correctly concluded by the authors that "this strongly suggests that it is the polymeric form that is present in fabrics dyed with indigo." Less justified appears the further conclusion that "this further deepens the mystery surrounding the nature of the forces that hold dyes of this type to fibers. . . ."

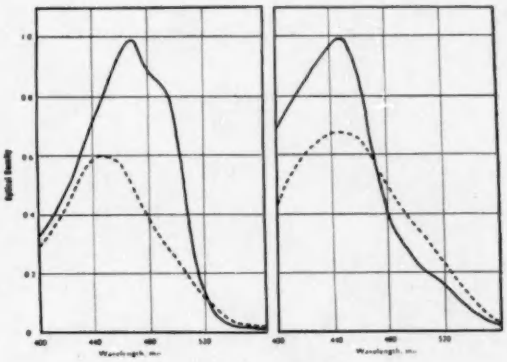

Fig. 10. Light absorption by Caledon Yellow 3G (left) and Caledon Gold. Broken line; before soaping. Unbroken line; after soaping. Sumner, Vickerstaff, and Waters [22].

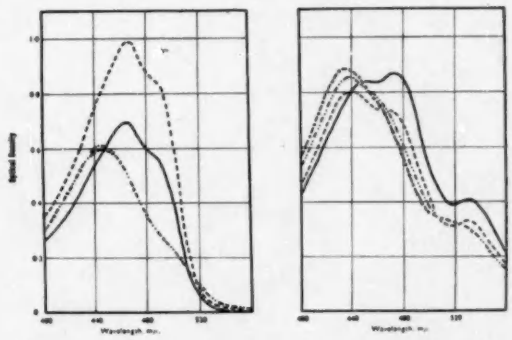

Fig. 11. Absorption of polarized light by Caledon Yellow 3G (left) and Caledon Brilliant Violet R. Sumner, Vickerstaff, and Waters [22].

Unsoaped

-x-x-x-x-x- Parallel

- - - - - -

Perpendicular

Soaped

The investigation of indigo dyed films and fibers by X-ray diffraction showed many years ago [23] that after oxidation of the leuco form, indigo is always present in crystalline form on the fiber (Figure 14). The spectrophotometric findings quoted only confirm this. Attraction forces must operate between fiber and dye to account for the exhaustion of the leuco dye from solution. After insolubilization by oxidation and subsequent crystallization, the cohesive forces between the dye molecules and the cohesive forces between the fiber molecules make difficult if not impossible the removal of the dye particles formed in the interior of the fibers. There is no need for assuming adhesion forces between dye particles and fiber. As a matter of fact, even if they would be present, such adhesion forces would operate only on the surface of the dye particles and could not be detected by optical methods, since the surface of the crystals contains only a small fraction of the dye molecules.

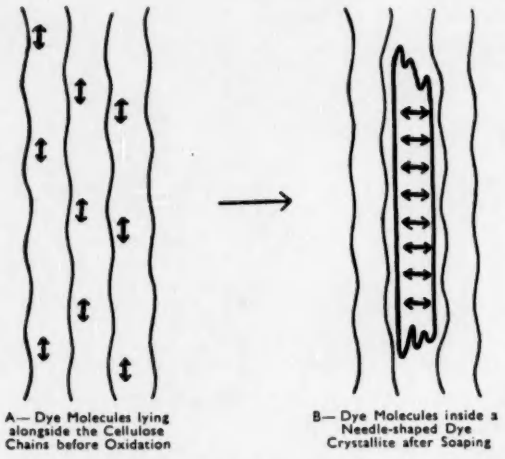
A— Dye Molecules lying alongside the Cellulose Chains before Oxidation
B— Dye Molecules inside a Needle-shaped Dye Crystallite after Soaping

Fig. 12. Orientation of vat dyes on cellulose. (A) before oxidation; (B) after oxidation. Sumner, Vickerstaff, and Waters [22].

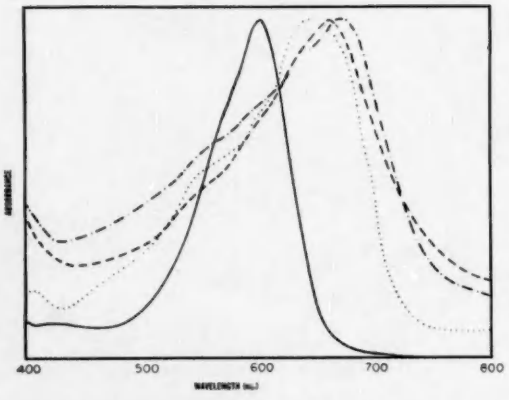

Fig. 13. The visible spectrum of indigo (.....) as a sublimed film; (————) in chloroform solution; (- - - -) as a pellet in KBr, and (-.-.-.-.-) in aqueous suspension. Dyed cellulose film gives maximum at 662 mμ. Weinstein and Wyman [28].

Interaction of Cellulose Dyes in the Fiber with Cationic Surfactants

Another interesting transformation which takes place in fibers is the interaction of the dyes with cationic surfactants, that is, with higher molecular weight amines and ammonium compounds. These are applied either to increase the wetfastness of the dyeings or the softness of the fabrics. Both dye fixing agents and cationic lubricants tend to decrease the light fastness of the dyes and to shift their shade. The most satisfactory explanation of these effects is based on the so-called salt formation between the cationic agent and the dye. More precisely described, the process is that of ion exchange. Originally, the direct dyes are held by the cellulose in the form of colored anions. Their colorless gegenions, usually sodium, are held by electrostatic forces in the form of a diffuse ionic layer. As the surfactant penetrates into the fiber, the sodium ions are gradually replaced by the high molecular cations. This

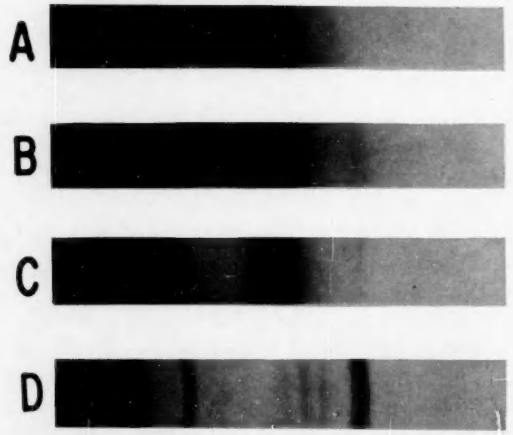

Fig. 14. X-ray diagram of indigo. Top: cellulose film, undyed, second: cellulose film, dyed, not aftertreated; third: cellulose film, dyed, aftertreated; bottom: indigo crystals. Susich and Valko [23].

process, by itself, does not change the state of adsorbed dye. However, the salt formed by the cation of the surfactant and the anion of the dye is insoluble. Therefore, the bulk phase in equilibrium with the monolayer is not the aqueous solution of the dye as it was before, but a crystalline or amorphous solid formed by combination of these two large ions. This situation gives the condition for the collapse of the monolayer. It this occurs, light fastness and light absorption of the dye are bound to change [8].

The investigation of the state of the dyes and of their transformations in cellulosic fibers is still in its infancy. Combination of techniques such as X-ray, spectrophotometry, and electron microscopy should be able to shed light not only on the mechanism of dyeing and finishing but also on many aspects of the submicroscopic structure of fibers.

Utility of Theory of Dyeing

The purpose of the theory of dyeing is not only to satisfy intellectual curiosity but also to control scientifically the dyeing process.

The theory of absorption equilibrium of dyeing cannot yet pride itself with spectacular contributions to actual dyeing practice. The theory of substantivity is not yet capable of providing definite direction toward the synthesis of more substantive dyes. The explanation of the salt effect did not lead immediately to better utilization of Glanber's salt in dyeing. The determination of diffusion coefficients has not yet helped to accelerate the dyeing cycle.

Even though no practical benefits of the modern theory can be dramatically demonstrated, it is in fact exerting increasing influence. To mention a few such effects, the classification of direct dyes in terms of their level dyeing, their salt sensitivity, and their temperature dependence and the systematic use of this classification for selection of the dyes in order to achieve optimum performance and compatibility, are greatly aided by the understanding of the mechanism of dyeing in terms of equilibrium and rate. Likewise, optimum use of leveling agents is made easier by learning the mechanism of their functioning. Scientific approach to such problems as package dyeing is facilitated by using the principles of kinetics of dyeing [4].

The fundamentals of the modern theory of dyeing were established 20 years ago. The intervening two decades have brought refinements of the theory in some details and demonstrated its applicability to many specific problems. Gradually they brought the theory its general recognition. As the validity of the theory is generally acknowledged and as it is accepted as the basis for teaching and learning the technology of textile dyeing, the process of supplanting the empirical craft of dyeing by scientifically controlled methods is bound to gain speed.

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Correction

In "The Interpretation of Creep Failure in Textile Fibers as a Rate Process," by Coleman and Knox (**27**, 393–399), there is an error in Equation *22b*; the right-hand member should read $\frac{-1}{B'} \ln (1 - t_F/t_B)$.

INDUSTRIAL SECTION

Melange or Vigoureux Printing of Wool: A Method for Increasing the Rate of Dye Fixation

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Abstract

The steaming time required for dye fixation has been reduced from the generally accepted 1 or 2 hrs. at atmospheric pressure to a matter of minutes by the use of suitable solvents in the printing paste and by increasing the steam pressure.

For example, with 5–10% benzyl alcohol in the paste, most neutral dyeing premetallized and many acid dyes required 5–15 min. steaming at 5–10 lb./sq. in. Chrome dyes required somewhat longer.

Besides increasing the rate of fixation, suitable solvents increased the depth of color obtained for a given amount of dye.

Introduction

The Melange process consists of printing a sliver with a series of colored bands. The spacing is such that each fiber has several colored and white sections, so that a very even mixture effect can be obtained in subsequent gilling. It is impossible to obtain the same degree of evenness by blending white and dyed slivers. The historical aspects of the process, the various operations and machinery, and typical printing paste recipes have been described recently by a number of authors [1, 2, 5, 7, 8, 17, 19, 20]. Pattern cards and circulars of dyestuff manufacturers also describe the method and give recipes.

The typical procedure, which does not appear to have changed much in the century that it has been known, is to pass wool top through a gill box attached to the printing machine. The thin sliver, about 18 in. wide, is then passed between a fluted roller and a felt covered roller saturated with printing paste. Only those portions of the sliver pressed into the felt by the flutes become coated with paste. The sliver is then allowed to build up into bundles about 1 yd. square and 18 in. high. These are wrapped in cloth and steamed on trays in a cottage type steamer to fix the dye. Normal steaming procedure is either a single 1-hr. period at atmospheric pressure or two such periods separated by an interval of 1 hr. After cooling, usually overnight, the sliver is backwashed to remove unfixed dye, thickener, etc.

Such long periods for dye fixation tend to create a bottleneck in the process; in addition, with alkaline slivers there is the possibility of damage in the unprinted sections [15]. The purpose of this work was to overcome these disadvantages.

Three ways of decreasing the fixing time were investigated—pretreatment of the wool, modification of the printing paste, and alteration of the conditions for dye fixation.

Materials and Methods

Wool

Commercially prepared 60's quality Merino top was used. Before printing it was reduced on a can gill to a sliver about 2 in. wide weighing 140–150 drams/40 yd. This was about half normal top weight, and the thickness was comparable with commercially printed sliver.

Pretreated top was produced by continuously padding through alcoholic KOH followed by a wait in a J-box, then rinsing with a rapid flow of water. Conditions were chosen to give the optimum degree of shrinkproofing (8% wt./vol. KOH in absolute ethanol, 23° C., 6 min. wait). Details of this process will be described elsewhere. Acidified top was prepared by padding through a dilute acetic acid solution, followed by rinsing with water. Solvent extracted top was prepared by padding through several baths of petroleum ether, the expressed liquid being discarded. All these tops were air-dried and reduced to the required weight as above.

Printing

No small scale melange printing machine has been previously described, although a method for laboratory printing of sliver with a hand block has been mentioned by Potter [17]. For this work a small printing machine with stainless steel rollers 3 in. wide was constructed (Figure 1). It was a scaled down model of a commercial machine, except that the felt covered roller dipped directly into the printing paste. This allowed the use of unthickened dye solutions when required. The fluted roller was cut to give a 50% cover ($\frac{1}{2}$ in. bands, $\frac{1}{2}$ in. spacings).

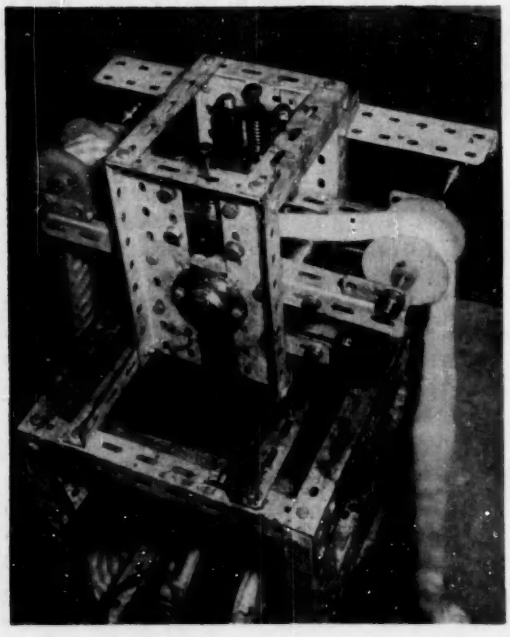

Fig. 1. Laboratory size melange printing machine.

About 100 ml. of dye paste or solution was required for a run. A small machine of this type might prove very convenient and economical for matching shades in industry. Results obtained with the small laboratory machine were reproducible on a commercial machine. After printing, the sliver was cut into 24 in. lengths for steaming. A control (unsteamed) sample was taken every 5–6 lengths. To prevent drying of the paste, samples were stored in closed containers until steamed.

Printing Paste

Typical printing pastes contain the following ingredients: dye, thickener, an acid or its ammonium salt, glycerol, sodium chlorate, wetting agent, antifrothing agent, and, for chrome dyes only, a chromium salt.

During the course of this work the basic recipe was dye, acetic acid (3% vol./vol.), and water, with other additions as required. Commercial dyes were used; most of the results were obtained using Cibalan Black BGL because heavy shades take longer to fix and black is probably the most popular shade (for grey). The concentration of this dye in the printing paste was 4% wt./vol. unless otherwise stated. The thickener used was Solvitose H4M, an etherified starch derivative. When chrome dyes were used, the appropriate quantity of chromium fluoride (3–6%) was added.

The usual method of preparing the paste was to mix the solids and add them to the previously mixed liquids at 30–40° C., with stirring. In the absence of solvent most dyes were in suspension, but, as many were supplied as a very fine powder, it was not necessary to dissolve them separately in hot water first. In the presence of solvent only the chrome dyes were not completely dissolved. If the particle size of this type was too large, the dye was dissolved in hot water and added to the previously dissolved thickener, so that very small particles formed on cooling. This slurry and the other ingredients were then mixed. The thickener usually kept immiscible solvents dispersed for several hours. If any separation occurred on longer standing, the solvent was readily redispersed by shaking or stirring.

Steaming

Steaming at atmospheric pressure was done in a vessel with a loosely fitting lid and an open drain. The wool was placed on a wire screen under an in-

verted V-shaped metal hood which prevented condensed water from dropping on it. Pressure steaming was done in a small horizontal autoclave-type vessel which has been described previously [15].

Timing was started when the operating temperature was reached (about 1–2 min. after introducing the steam). After steaming for the required time, the lengths of sliver were conditioned at 65% R.H. and 70° F. before weighing samples for determining the amount of dye fixed.

Estimation of Dye Fixation

The procedure was to weigh 5 g. of printed sliver, add 100 ml. of aqueous ethanol at room temperature, and stir thoroughly several times during 15 min. A portion of the extract was filtered through a fluted paper and the dye concentration determined with a Hilger Spekker Absorptiometer. Unpurified dye in aqueous ethanol of the appropriate concentration was used to obtain calibration curves. Percentage fixation was expressed as

$$\left(1 - \frac{\text{dye extracted from steamed sliver}}{\text{dye extracted from unsteamed sliver}}\right) \times 100.$$

The amount of dye deposited on the wool was calculated assuming a 50% cover, and in the following sections refers to the amount of dye on the printed portions of the sliver.

Ethanol was used for the extraction of printed sliver because water gave cloudy solutions in which the dye concentration could not be determined colorimetrically. Some water had to be added to the ethanol to swell the thickener sufficiently to allow dissolution of occluded dye particles. Any concentration of aqueous ethanol between 25 and 75% extracted all the dye and gave a clear solution after filtration. For most dyes, 70% ethanol was used because filtration was faster. More dilute ethanol was used when the dye was less soluble in this solvent than in water. Further extraction of ethanol-extracted slivers at 40° C. with dilute aqueous $NaHCO_3$ containing wetting agent did not remove more dye.

Chrome dyes were not estimated in the above way, as they were not sufficiently soluble in aqueous ethanol, and the amount of complex formation was not known; dye fixation and development of color were both estimated visually. Sliver was extracted as above at 40° C. with 100 ml. of 0.5% $NaHCO_3$ solution containing wetting agent. Fixation was considered satisfactory if the depth of color of the extract was similar to an extract from a sliver printed with a premetallized dye of similar color with about 95% of the dye fixed. Development was considered satisfactory if no further change in color occurred on longer steaming.

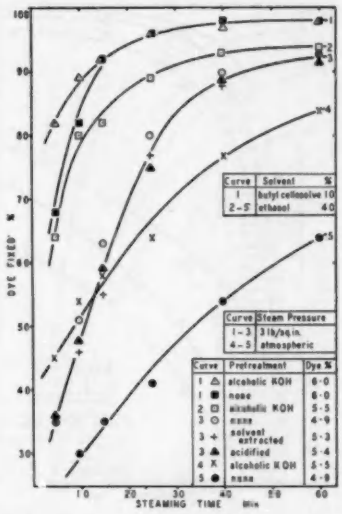
DYE FIXED %
STEAMING TIME Min
Curve | Solvent | %
1 | butyl cellosolve | 10
2–5 | ethanol | 40
Curve | Steam Pressure
1–3 | 3 lb/sq.in.
4–5 | atmospheric
Curve | Pretreatment | Dye %
1 | alcoholic KOH | 6·0
1 | none | 6·0
2 | alcoholic KOH | 5·5
3 | none | 4·9
3 | solvent extracted | 5·3
3 | acidified | 5·4
4 | alcoholic KOH | 4·5
5 | none | 4·9

Fig. 2. Effect of pretreatment of wool on rate of fixation of Cibalan Black BGL (4% wt./vol. in paste). Throughout this work percent dye refers to the amount of dye on the printed sections of the sliver.

Results and Discussions

Pretreatment of the Wool

It is well known that a pretreatment capable of modifying the surface of the wool increases the rate of dyebath exhaustion. Wet chlorination pretreatment is used to increase the rate of dye fixation in printing of wool cloth [11]. Most authors consider such a pretreatment unsuitable for melange printing because it is said to have a detrimental effect on subsequent processing.

Figure 2 shows the effect on rate of dye fixation of alcoholic KOH treatment, solvent extraction, and acidification of the wool before printing.

As would be expected with the type of dye used (neutral-dyeing premetallized), pre-acidification had little effect.

Solvent extraction had no effect. This was unexpected, as general opinion is that oil interferes with dye fixation.

Alcoholic KOH pretreatment increased the rate of fixation (Curves 4 and 5, Figure 2), as would be

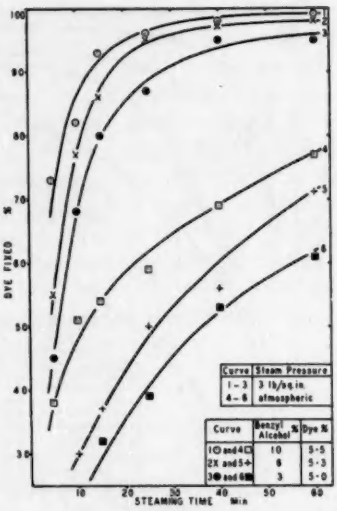
DYE FIXED %
STEAMING TIME Min
Curve | Steam Pressure
1 - 3 | 3 lb/sq.in.
4 - 6 | atmospheric
Curve | Benzyl Alcohol % | Dye %
1○ and 4□ | 10 | 5-5
2X and 5+ | 6 | 5-3
3● and 6■ | 3 | 5-0

Fig. 3. Effect of benzyl alcohol on rate of fixation of Cibalan Black BGL (4% wt./vol. in paste).

expected. However, this effect was of significance only if the printing paste contained a relatively ineffective solvent and steaming was done at low pressures. As the pressure was increased (Curves 2 and 3) the effect became less marked; when a more effective solvent was used (Curve 1), the difference between treated and untreated became negligible. Therefore, there is no point in pretreating the wool, as the rate of dye fixation can be increased much more conveniently and to a greater extent by the use of a suitable solvent in the paste or by increasing the steam pressure. Karrholm and Lindberg [10] observed a similar effect when dyeing in the presence of amyl alcohol; pretreatment increased the rate of exhaustion but not as much as the use of solvent; in the presence of solvent, pretreatment was without effect on the rate of exhaustion.

Modification of the Printing Paste

Many recipes appear to be unnecessarily complicated, and some ingredients are used without adequate justification. The effect of some of the more common printing paste constituents has been determined.

Antifrothing agents. Printing pastes prepared according to normal recipes froth considerably in use. Therefore, an antifrothing agent, frequently oil of turpentine, is used. Pastes containing any of the solvents used here did not froth even with normal amounts of wetting agents. Therefore, an antifrothing agent would not be required in the modified paste developed in this work.

Sodium chlorate. This occurs in almost all printing paste recipes. It is supposed to "improve the yield," which presumably means to increase the rate of fixation or depth of color, probably by modifying the wool. It is also supposed to prevent "reduction of the dye by the wool or thickener during steaming." If any reduction does occur it is more likely to be due to the oxalic acid frequently used in pastes; oxalic acid is therefore considered an unsuitable ingredient. Table 1 shows that $NaClO_3$ had no effect on rate of fixation; neither did it appear to have any effect on the depth of color. Therefore, it was considered to be an unnecessary constituent and was omitted from the modified recipe.

Glycerol. It is generally accepted that dye fixation is retarded if the paste dries out on the sliver before steaming. Glycerol, because it is hygroscopic, is often used in the paste to prevent this effect.

Figure 4 shows that glycerol had no effect on the rate of dye fixation. To confirm that drying retards fixation and determine whether hygroscopic solvents prevent it, sliver was printed with pastes containing various solvents, some of which were hygroscopic. After printing, one set of sliver lengths was stored in a closed container and the other dried in a current of cool air for 1–2 hr. before steaming. Table II shows that drying caused a considerable reduction in fixation with and without solvent. Glycerol prevented this only to a very slight extent, if at all. With a paste containing butyl cellosolve, diethylene glycol, which is hygroscopic, appeared to be slightly more effective. However, this was more likely due

TABLE I. Effect of Sodium Chlorate on Rate of Dye Fixation

Dye,* 3.5% wt./wt. Cibalan Black BGL (4% wt./vol. in paste); $NaClO_3$, 0.5% wt./vol.; steam pressure, 3 lb./sq. in.

Steaming time, min.	Dye fixed, %	
	With $NaClO_3$	Without $NaClO_3$
5	35	33
15	63	63
25	74	72
40	82	80

* Throughout this work the percent dye on the wool is expressed as the amount of dye on the printed section only, assuming a 50% cover.

to its solvent effect on the dye (see Figure 4) and its low volatility rather than its hygroscopic effect. Cyclohexanol [14] is also hygroscopic, and in addition a good dye solvent (Figure 4), but it did not prevent the drying effect sufficiently to warrant its use for this purpose. Therefore, the use of hygroscopic solvents is relatively useless in melange printing, where the sliver is steamed wet and not much drying occurs after printing. However, in view of the results in Table II, it is most important to reduce this drying to a minimum.

In practice it was found that drying was confined to a very small amount of wool on the outside of the sliver bundle, and would be of little consequence with acid or premetallized dyes, as the final shade was not affected. However, with chrome dyes, drying also retarded development of color; although it was still confined to the outside of the bundle, it was sufficient to alter the final shade after blending. Hygroscopic solvents did not prevent this. It occurred when the sliver bundle was allowed to stand for too long (1–2 hr.) or too short (< 5 min.) a time before steaming. The former was obviously due to evaporation and the latter most likely to volatilization of the solvent in the steamer before it had time to be adsorbed on the wool. In either case it was prevented most effectively by wrapping the bundles in damp cloths. It is common practice to use dry cloths; Gurtler [7] mentions the use of wet ones.

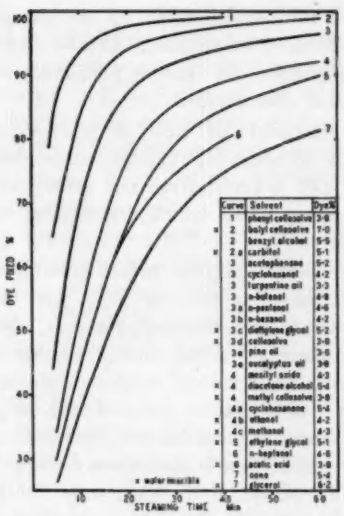

Fig. 4. Effect of various solvents (10% vol./vol. in paste) on rate of fixation of Cibalan Black BGL (4% wt./vol. in paste). Acetic acid 3% vol./vol. in all pastes except curve 6 (10%). Steam pressure, 3 lb./sq. in. Letters after curve numbers indicate that those solvents gave curves below the one shown in the order listed.

Thickener. Thickener is used in printing paste to facilitate transfer of paste from the color box to the felt covered roller and to prevent spreading of the print on the sliver. However, printing was done on both laboratory and commercial machines with unthickened dye solutions by raising the color box until the felt covered roller dipped directly into the solution; no appreciable running of the print occurred. It was expected that the thickener would reduce the rate of dye fixation, but Table III shows that it had no effect in the presence of solvent. Although thickener was not necessary with water miscible solvents, it very effectively dispersed water immiscible ones and chrome dyes, which were not completely dissolved even in the presence of solvent. Therefore, it was considered advisable to retain the thickener in the paste recipe.

Acid. Almost every common organic acid or a salt which decomposes on steaming has been suggested as suitable for printing pastes. The relative merits of the various acids were not investigated, because most dyes with a sufficiently high wash fastness to be suitable for printing will dye wool under mildly acid conditions. Therefore, it was considered

TABLE II. Effect of Drying Before Steaming and the Effect of Hygroscopic Solvents

Dye, Cibalan Grey BL (2.5% in paste)
Steamed 30 min. at atm. pressure

Solvent	% vol./vol.	Dye % wt./wt.	Dye fixed, % Dried sliver	Dye fixed, % Undried sliver
None		1.6	40	60
Glycerol	5	1.7	43	58
Ethanol	20	1.5	48	84
Ethanol + glycerol	20 5	1.5	55	87

Dye, Cibalan Black BGL (4% in paste)
Steamed 15 min. at 3 lb./sq. in.

Solvent	% vol./vol.	Dye % wt./wt.	Dye fixed, % Dried sliver	Dye fixed, % Undried sliver
Butyl cellosolve	10	3.7	29	89
Butyl cellosolve + diethylene glycol	5 5	3.6	43	92
Cyclohexanol	10	4.2	42	78

that acetic acid, which is one of the cheapest available, would be quite suitable. Oxalic acid was considered unsuitable for reasons previously mentioned (see *Sodium chlorate*).

From the point of view of rapid fixation and prevention of steaming damage, it is desirable to have the pH lowered from the start; there is no point in using a salt which decomposes to an acid on steaming.

Wool is usually alkaline before printing, therefore subject to steaming damage [15]. As it was intended to use higher steaming pressures, which would accelerate damage, it was considered that if a volatile acid was used the pH of the unprinted parts of the sliver might also be reduced and so protected. Acetic acid was suitable from this point of view also; Table IV shows that it does reduce the pH of both parts of the sliver. It is surprising that this effect occurred before steaming. It will be seen that 2% acetic acid was sufficient, but this would vary with the amount of alkali on the wool; 3% was considered to be a suitable quantity for the modified paste.

TABLE III. Effect of Thickener on Rate of Dye Fixation

Dye, Cibalan Black BGL (4% in paste); thickener, Solvitose H4M; steam pressure, 3 lb./sq. in.

Solvent	% vol./vol.	Dye % wt./wt.	Thickener % wt./vol.	Dye fixed, % after 10 min.	15 min.	25 min.
Butyl cellosolve	10	7.0	4	77	95	99
			0	80	95	99
Butanol	10	4.9	4	72	85	96
			0	67	86	96
Ethanol	20	4.0	4	59	86	94
			0	54	83	92

TABLE IV. Effect of Acetic Acid in Printing Paste on pH of Aqueous Extract of Printed Sliver

liquor/wool, 100/1

Sliver	pH for acetic acid concentration (vol./vol.) of 1%	2%	3%
Before printing	9.1	9.5	9.0
Printed section unsteamed	7.2	6.1	6.8
White section unsteamed	7.2	6.2	6.6
Printed section steamed	7.3	6.8	6.8
White section steamed	7.5	6.7	6.7

To determine whether the acid did retard steaming damage, printed sliver was steamed at various pressures until yellowing was noticeable on the unprinted sections; Table V shows the time required (see also [15]). By comparison with Table XI it will be seen that, in the presence of acid, yellowing did not occur until the sliver had been steamed for about twice as long as it took to fix dyes with the slowest rates. Therefore, no fiber weakening should occur when the sliver is steamed for long enough to fix the dye. To confirm this, sliver was printed with a chrome dye (this type has the slowest rate) with 3% acetic acid in the paste and steamed at several pressures for long enough to fix the dye. The slivers were rinsed with warm water to remove thickener etc. and conditioned at 65% R.H. and 70° F. before determining fiber breaking strengths and elongation at break on a Cambridge Extensometer. Statistical examination of the results in Table VI showed no significant change in these fiber properties due to the steaming treatments.

At no stage was it considered practical to print with a paste containing no acid; therefore, rates of fixation in the absence of acid were not determined.

Solvents. The main feature of the modified paste is the use of suitable solvents. Solvents have been mentioned previously in paste recipes for getting the dye into solution [2, 19]. Diserens [6], Mellan [14], and solvent manufacturers' literature list a large number, including some of the lower aliphatic alcohols, as suitable for this purpose in dyeing and printing. Lister [12] also mentioned the use of ethanol, which was the first solvent tried in this work because of its low cost and good solvent effect on premetallized dyes.

TABLE V. Approximate Steaming Times at Different Pressures to Cause Yellowing of White Sections of Printed Sliver

With and without 3% acetic acid in printing paste

Pressure, lb./sq. in.	Time, min. With acid	Without acid
3	>90	60
7	>60	30
10	40	15
20	20	5*
30	5*	1*

* Fibers contracted in length when steamed approximately twice these times.

Because of the high concentration of dye in the printing paste, much of it is usually in suspension. Initially it was supposed that solvents would increase the rate of dye fixation by getting the dye into solution and, as a result of this, by more even distribution of the dye on the wool (see *Effect of Dye Concentration* below). Therefore, it was considered that any water miscible dye solvent would be suitable. However, when Peters and Stevens [16] published their results on the use of immiscible solvents such as butanol for low temperature dyeing, it appeared that better results could be expected with dye solvents only slightly miscible with water. Such solvents would extract most of the dye from the water and would be taken up preferentially by the wool. The resulting increase in the dye concentration gradient across the wool surface should thus increase the rate of fixation.

The volatility of the solvent was considered to be important, because a highly volatile solvent would be lost too soon during steaming with a consequent reduction in rate (see section on steaming).

A preliminary selection of solvents was made by determining the solubility or distribution of dye in a mixture of solvent and water containing a small quantity of acetic acid. Most neutral dyeing premetallized dyes were soluble to some extent in most common solvents except hydrocarbons. The solubility of Cibalan Black BGL was chosen as the basis for selection of solvents, because it was found if a solvent dissolved this dye it dissolved all other premetallized dyes of this type. The partition of Cibalan Black between various solvents and water, compared with that of other premetallized dyes, indicated that this dye was more hydrophilic than the others. Therefore, a solvent selected using this dye should also be suitable for some acid dyes, and would have wider application than some of the more hydrophobic solvents such as thymol (used by Peters & Stevens [16] for low temperature dyeing with Cibalan Grey BL) or *o*-dichlorobenzene (used by Lister [13] with Lanasyn dyes), which only dissolve some premetallized dyes.

Printing experiments were done only with those solvents which might be suitable for commercial use from the point of cost, availability, and, most important, toxicity. Many of those shown in Figure 4 would hardly be suitable from the latter consideration.

Sliver was printed with pastes containing 4% wt./vol. Cibalan Black BGL, 3% vol./vol. acetic acid, 4% wt./vol. thickener, and a range of solvent concentrations up to 15% vol./vol. Steaming was done at atmospheric pressure and at 3 lb./sq. in. gauge. Figure 3 shows a typical set of results for benzyl alcohol.

The results for a number of solvents are collected in Figure 4. To avoid confusion, experimental points and many individual curves are not shown, the relative positions being indicated only in the key. Where one curve is assigned to more than one solvent, the experimental values did not vary by more than a few percent on either side. The results for 10% vol./vol. of solvent are given. The maximum effect was generally obtained with about this amount, except with ethanol, which gave slightly better results with 20–60%. With many of the solvents the maximum increase in rate was obtained with even less solvent; generally 10% was required to give the maximum increase in depth of color.

The increase in depth of color brought about by some solvents with the same amount of dye on the wool was most spectacular; from a practical point of view it is probably just as important as the increase in rate of fixation. This effect was not shown by water miscible solvents.

It will be seen (Figure 3) that with lower concentrations of solvent less dye was deposited; the amount varied with different solvents (Figure 4). This was probably due to the fact that addition of increasing amounts of solvent resulted in more complete wetting of the wool by the printing paste. The behavior of different solvents varied in this respect. Water immiscible solvents were effective in concentrations slightly greater than that required to satu-

TABLE VI. Effect of High Pressure Steaming on Fiber Strength

Sliver printed with Fast Chrome Black A150 as for Table XI. Number of tests (n) = 50

Steaming treatment		Mean breaking load, g.	Standard error (95% limit) $\frac{ts}{\sqrt{n}}$, g.	Mean elongation at break, %	Standard error (95% limit) $\frac{ts}{\sqrt{n}}$, %
Pressure, lb./sq. in.	Time, min.				
Unsteamed	—	5.7	1.4	32	7
10	25	6.5	0.8	28	6
20	10	5.5	1.0	30	7
30	3	6.4	0.7	40	7

rate the aqueous phase (*e.g.*, 10% butanol), whereas large quantities of water miscible solvents were required (*e.g.*, 40% ethanol).

The machine settings were left the same when doing a run with different concentrations of a solvent, so that more dye was usually deposited with the higher concentrations. When any attempt was made to compensate for this effect when different solvents were used, the tendency usually was to overcompensate because of the poor appearance of the print with relatively ineffective solvents and the excellent appearance with effective solvents. For example, 3.4% dye with phenyl cellosolve[1] gave a darker and more even print than about 5% dye with any of the solvents from Curve 4 (Figure 4) or lower.

It will be seen that a considerable increase in the rate of fixation resulted from the use of solvents. Phenyl cellosolve was superior to the other solvents, but too expensive for commercial use. Benzyl alcohol and butyl cellosolve are both cheap; butanol, although it was less effective, was also considered because of its relatively low cost. Other solvents relatively effective in increasing the rate either did not increase the depth of color (carbitol,[2] oil of turpentine) or had some unpleasant characteristic. Benzyl alcohol is less toxic than butyl cellosolve but more so than butanol [18]; its low volatility (BP. 205° C.) should make it safe to use. All three solvents were used extensively during this work. Although the odor of butyl cellosolve was innocuous, it was found to have somewhat unpleasant aftereffects. The irritating effect of butanol on the respiratory system, even in concentrations considered safe, is well known. No ill effects were observed with benzyl alcohol; in addition, its odor is quite mild. Therefore, benzyl alcohol was considered most suitable for commercial use, even though it costs more than the other two. From Figures 3 and 8 and Table IX, suitable concentrations were considered to be 5–10%, depending on the amount of dye.

The number of solvents examined was by no means exhaustive; it is possible that solvents more effective than benzyl alcohol could be found. For example, it is possible that higher members of the carbitol series would be very effective (compare with cellosolve series in Figure 4), but none of these were available when this work was in progress.

[1] Cellosolves, also called oxitols, are monoethers of ethylene glycol.

[2] Carbitols are monoethers of diethylene glycol.

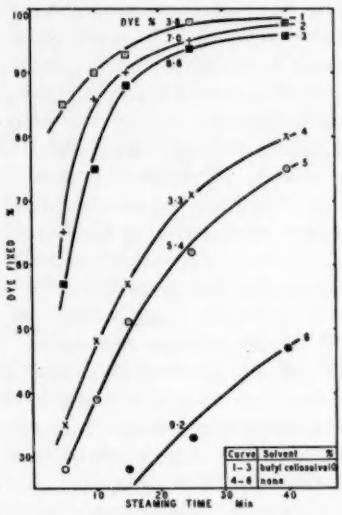

Fig. 5. Influence of solvent on the effect of dye concentration. Dye, Cibalan Black BGL (4, 6, and 8% wt./vol. in paste); steam pressure, 3 lb./sq. in. Dye % wt./wt. on printed part of wool marked on curves. Curves 2 and 3 were identical with those for 10% benzyl alcohol with 5.5% and 8.2% dye respectively.

Dye. EFFECT OF CONCENTRATION. It was found as expected (Figure 5) that increasing the amount of dye considerably increased the time required for fixation. Therefore, the effect of dye concentration had to be considered when assessing the effect of any other factor, particularly when relatively ineffective solvents were used. However, Figure 5 shows that when the rate of fixation was increased by the use of solvent, the effect of varying the dye concentration was much less marked. Increasing the steam pressure had a similar effect.

PREMETALLIZED AND ACID DYES. Having chosen benzyl alcohol as the most suitable solvent, sliver was printed with a number of different dyes in the presence of this solvent to determine which dyes could be satisfactorily applied by this method. A preliminary selection of dyes was made by determining qualitatively the partition between benzyl alcohol and dilute (0.5 *N*) acetic acid solution. The use of dilute acetic acid instead of water altered the partition of some dyes in favor of the benzyl alcohol. This would be expected if the dye was originally in the form of a salt. All the neutral dyeing premetallized type (Irgalans, Cibalans, Isolans, Lanasyns, and Ortolans) were completely extracted into the solvent layer, leaving the aqueous layer colorless.

The partition of acid dyes varied. Almost every dye of the acid milling class that was tried (*e.g.*, Carbolans and Coomassies, which have high wash fastness properties and would therefore be suitable for printing) was either completely absorbed in the benzyl alcohol layer or distributed very much in its favor. Many with good levelling properties and poor washfastness were distributed very much in favor of the aqueous phase, but some others in the same class were distributed in favor of the benzyl alcohol. Therefore, dyes suitable for printing should give partition ratios in favor of benzyl alcohol and be suitable for application by this method. However, the fact that a dye is more soluble in benzyl alcohol than in water does not necessarily mean that it has a sufficiently high wash fastness to be suitable for printing, although all dyes showing this property would give greater rates in the presence of this solvent. This is shown by the level dyeing group of dyes Naphthalene Scarlet 4RS, Naphthalene Red EAS, and Naphthalene Red JS, which differ only in the number of sulfonic acid groups (3, 2, and 1 respectively). These dyes have been used to dye wool in the presence of amyl alcohol [10], and, as would be expected, similar results were obtained here with regard to partition and rates of fixation (Figure 6). In the absence of solvent, these dyes gave different rates in the same order as in Figure 6, but the differences were of smaller magnitude; the rates for Naphthalene Scarlet 4RS in the presence and absence of solvent were the same.

The partitions of some of the acid dyeing premetallized type (*e.g.*, Neolans) were determined; most were distributed in favor of the aqueous layer, although on standing for several days there appeared to be a gradual transfer of dye to the solvent layer. Printing experiments were done with two dyes of this type with different partition ratios. Printing was also carried out with dyes selected from the other types mentioned above. Most dyes were chosen from the neutral dyeing premetallized range because of their obviously greater suitability; in this class, selection was completely random. The acid milling dyes were selected to cover a range of partitions between benzyl alcohol and water.

The concentration of dye in the paste was varied to cover the range normally encountered in printing (25–80 g./l.); 7.5% benzyl alcohol was used, although results obtained later showed (Figure 8, Table IX) that it could have been less for the light

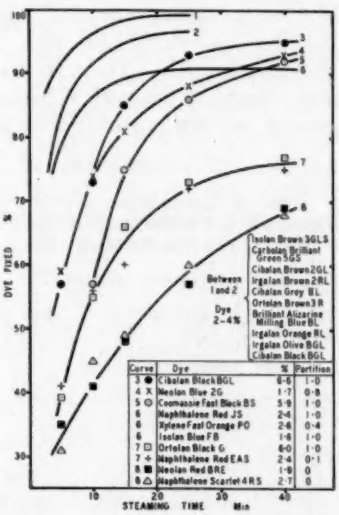
DYE FIXED %
STEAMING TIME Min
Between 1 and 2
Dye 2–4%
Isolan Brown 3GLS
Carbolan Brilliant Green 5GS
Cibalan Brown 2GL
Irgalan Brown 2RL
Cibalan Grey BL
Ortolan Brown 3R
Brillant Alizarine Milling Blue BL
Irgalan Orange RL
Irgalan Olive BGL
Cibalan Black BGL
Curve | Dye | % | Partition
3 ● Cibalan Black BGL 6·6 1·0
4 X Neolan Blue 2G 1·7 0·8
5 ○ Coomassie Fast Black BS 5·9 1·0
6 Naphthalene Red JS 2·4 1·0
6 Xylene Fast Orange PO 2·6 0·4
6 Isolan Blue FB 1·6 1·0
7 □ Ortolan Black G 6·0 1·0
7 + Naphthalene Red EAS 2·4 0·1
8 ■ Neolan Red BRE 1·9 0
8 △ Naphthalene Scarlet 4RS 2·7 0

Fig. 6. Rates of fixation of various dyes (blacks 8%, olive 4%, browns 3%, and others 2.5% wt./vol. in paste). Solvent, 7.5% benzyl alcohol; steam pressure, 3 lb./sq. in. The partition which varied with dye concentration is expressed as the fraction of dye in benzyl alcohol layer with equal volumes of aqueous and solvent phases both previously saturated with respect to one another; mean concentrations of dye, 0.25 g./l. and acetic acid, 0.25 *N*. The partition of all dyes between Curves 1 and 2 was 1.0, except for Brilliant Alizarine Milling Blue BL, which was 0.7.

The concentration of dye in the paste was varied to cover the range normally encountered in printing (25–80 g./l.); 7.5% benzyl alcohol was used, although results obtained later showed (Figure 8, Table IX) that it could have been less for the light

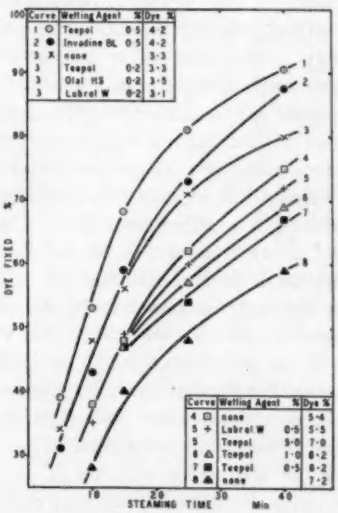
DYE FIXED %
STEAMING TIME Min
Curve | Wetting Agent | % | Dye %
1 ○ Teepol 0·5 4·2
2 ● Invadine BL 0·5 4·2
3 X none 3·3
3 Teepol 0·2 3·3
3 Olal HS 0·2 3·3
3 Lubrol W 0·2 3·1
Curve | Wetting Agent | % | Dye %
4 □ none 5·4
5 + Lubrol W 0·5 5·5
5 Teepol 5·0 7·0
6 △ Teepol 1·0 6·2
7 ■ Teepol 0·5 6·2
8 ▲ none 7·2

Fig. 7. Effect of wetting agents on rate of fixation of Cibalan Black BGL (curves 1–5+, 4% wt./vol.; curves 5–8, 8% wt./vol. in paste). No solvent; steam pressure, 3 lb./sq. in. Lissapol N (0.2%) and Lissapol C (0.2%), both with 3.5% dye, gave curves between 1 and 2.

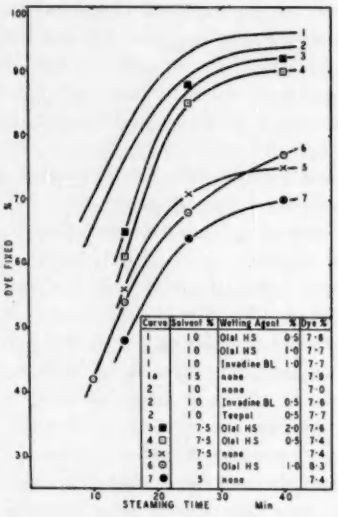
DYE FIXED %
STEAMING TIME Min
Curve | Solvent % | Wetting Agent | % | Dye %
1 | 10 | Olal HS | 0·5 | 7·6
1 | 10 | Olal HS | 1·0 | 7·7
1 | 10 | Invadine BL | 1·0 | 7·7
1a | 15 | none | | 7·8
2 | 10 | none | | 7·0
2 | 10 | Invadine BL | 0·5 | 7·6
2 | 10 | Teepol | 0·5 | 7·7
3 ■ | 7·5 | Olal HS | 2·0 | 7·6
4 □ | 7·5 | Olal HS | 0·5 | 7·4
5 × | 7·5 | none | | 7·4
6 ⊙ | 5 | Olal HS | 1·0 | 8·3
7 ● | 5 | none | | 7·4

Fig. 8. Effect of wetting agents on rate of fixation of Cibalan Black BGL (8% wt./vol. in paste). Solvent, benzyl alcohol; steam pressure, 3 lb./sq. in. Curve 1a was between curves 1 and 2.

shades and more for the heavier shades. The other paste constituents were as shown in Table XI. Steaming was done at 3 lb./sq. in. pressure.

The results in Figure 6 show that fixation of low concentrations of the neutral dyeing premetallized and acid milling types with a favorable partition between benzyl alcohol and water was very rapid and did not vary much with different dyes (Curves 1 and 2). The rates for Cibalan Black BGL (Curve 3) and Coomassie Fast Black BS (Curve 5) were quite normal, considering the dye concentration. The position of Xylene Fast Orange PO would be expected because of its low partition, but that of Isolan Blue FB (both Curve 6) appears to be abnormal; on the other hand, for both dyes and also for Naphthalene Red JS it was not the rate but the amount of dye fixed at equilibrium that was low. This would also appear to be the case with Ortolan Black G (Curve 7). The rate for Neolan Blue 2G (Curve 4) was quite good, considering that this type usually requires a much lower pH than used here. The low rate of Neolan Red BRE (Curve 8) is to be expected from its partition, which was completely in favor of the aqueous phase. Therefore, it would appear that all the neutral-dyeing premetallized and most acid milling dyes could be applied with advantage by this method.

CHROME DYES. The solubility of this type in both benzyl alcohol and water in the presence of acetic acid was very low, although the partition was usually in favor of the benzyl alcohol. Complex formation by boiling in the presence of chromium fluoride appeared to alter the partition slightly in favor of the benzyl alcohol. It is well established that chrome dyes require longer steaming for fixation; in view of their low solubility, spectacular increases in the rate were not expected from the use of solvents. However, preliminary experiments were sufficiently promising to warrant further investigation. Besides rate of fixation, rate of development and final depth of color were considered. The use of Neovadine AN [4], a nonionic levelling and/or stripping agent, for increasing the depth of color of these dyes has been suggested. The mill at which full scale trials were done had been using it for this purpose in conventional pastes. It would be expected that this type of compound would decrease the rate of fixation. This was found to be the case with Cibalan Black BGL; very little increase in depth of color resulted from its use with this dye. Table VII shows that, with a chrome dye in the presence of benzyl alcohol, the depth of color was increased, but the fixation reduced with increasing amounts of Neovadine AN. The reverse effect was obtained with increasing amounts of benzyl alcohol. The best balance between rate of fixation and devel-

TABLE VII. Effect of Concentration of Benzyl Alcohol and Neovadine AN on Fixation and Development of Color of Fast Chrome Black A150

Dye, 60 g./l. in paste; steam pressure, 7 lb./sq. in.

Benzyl alcohol, %	Neovadine, %	Steamed 30 min.		Steamed 40 min.	
		Color	Fixation	Color	Fixation
3	0	+	?	+	+
6	0	+	+	+	+
10	0	−	+	−	++
15	0	−	++	−	++
3	0.5	++	+	++	++
3	1.0	+++	−	+++	−
6	0.5	+	?	+	+
6	1.0	++	−	++	−
10	0.5	−	+	−	+
10	1.0	+	?	+	?
10	2.0	++	−	++	−
15	0.5	−	++	−	++
0	0.5	?	−	+	+
0	0	−	−	−	−

− unsatisfactory, ? doubtful, + satisfactory, ++ very good.

opment of color was obtained with 3% benzyl alcohol and 0.5% Neovadine AN. Similar experiments were done with butyl cellosolve and butanol, but benzyl alcohol gave superior results. The depth of color obtained with 3% benzyl alcohol and 0.5% Neovadine AN in the paste was far superior to that obtained with the conventional paste.

Sliver was then printed with a number of chrome dyes and samples steamed for a range of times at different pressures to determine the conditions required for satisfactory fixation and development.

The results in Table VIII indicate that the times were similar for all dyes even though they are not compared at the same concentration. It is likely that the rate-determining factor was diffusion of chromium into the wool. The steaming times considered necessary at different pressures are included in Table XI.

The appearance of sliver printed with chrome dyes was usually less uniform than that printed with acid or premetallized dyes. As the wash fastness of the latter are generally satisfactory and their rates of fixation greater, it is considered that they are to be preferred to chrome dyes for printing.

Wetting agents. Wetting agents are frequently used in printing pastes to promote wetting of the wool. Figure 7 shows that low concentrations (0.2%) of several wetting agents had little effect (Curve 3) on the rate of fixation of Cibalan Black BGL, while higher concentrations increased the rate somewhat (Curves 1 and 2). Comparison with Figure 4 shows that the increases were less than that obtained with ethanol. The depth of color was also slightly increased. It is interesting to note that the higher concentration of Lubrol W (nonionic) decreased the rate (Curves 4 and 5). Curves 5, 6, 7, and 8 show that large increases in the amount of wetting agent did not lead to proportionate increases in the rate.

Figure 8 shows the effect of some anionic agents in the presence of benzyl alcohol with a high concentration of dye. In the presence of this solvent, the wetting agents had no effect on depth of color. It will be seen that with 10% and 5% benzyl alcohol the effect of wetting agent was slight, but with 7.5% quite a large increase in rate resulted. However, this effect was not shown with the Ortolan or Coomassie Blacks of Figure 6.

As the rates of fixation of low concentrations of premetallized dyes were very high in any case, it was not expected that wetting agents would have much effect. This is confirmed in Table IX, which also shows that the concentration of solvent could be reduced without reducing the rate unduly. However, with concentrations below 5% the depth of color was reduced appreciably. The wetting agent had no effect on the depth of color.

The only case observed of a substantial increase in rate resulting from the use of a wetting agent was with Cibalan Black BGL in the presence of 7.5% benzyl alcohol. Therefore, in view of the slight increases obtained with other concentrations and other dyes, the use of any of the common anionic wetting agents (say 0.5–1%) could be considered optional.

TABLE VIII. Steaming Times at Different Pressures for Satisfactory Fixation and Development of Color of Different Chrome Dyes

Paste contained benzyl alcohol, 3%; Neovadine AN, 0.5%

Dye	g./l.	Time (min.) for steam pressure of 3 lb./sq. in.	7 lb./sq. in.	10 lb./sq. in.
Omega Chrome Brilliant Blue B	25	60	30	15
Diamond Chrome Fast Brown TBL	30	60	30	15
Solochrome Red ERS	25	>60	30	20
Chrome Fast Black FBW	80	—	20	15
Solochrome Black WDFA	80	—	40	25
Fast Chrome Black A150	60	>60	35	25

TABLE IX. Effect of Concentration of Benzyl Alcohol and Olal HS on Fixation of Irgalan Brown 2GL

Dye in paste, 4% wt./vol.; steam pressure 3 lb./sq. in.

Benzyl alcohol, % vol./vol.	Olal HS, % vol./vol.	Dye on wool, % wt./wt.	Dye fixed, %, after 10 min.	25 min.	40 min.
7.5	0	2.3	96	97	97
5.0	0	2.9	92	92	96
3.0	0	2.4	90	95	96
3.0	0.5	2.7	89	94	94
1.0	0	2.1	81	93	93
1.0	0.5	2.2	88	92	93

Conditions for Dye Fixation

Steaming the wool at atmospheric pressure (usually for two periods of 1 hr. each) to fix the dye is common practice. Although steam under pressure is frequently used with synthetic fibers [9], only rarely

is the use of steam under pressure advocated for wool [1, 7]. Nicholls (unpublished) has shown that steaming at higher pressures increased the rate of dye fixation; results given here confirm this.

Although increasing the steam pressure was the obvious way of increasing the rate of dye fixation, some preliminary experiments were carried out to examine other methods of dye fixation. Results of these are given in Table X.

It is seen that superheated steam reduced fixation by its drying effect; once the wool was dried completely, probably no further fixation of dye would occur. Therefore it is most important that the steam should be saturated. This drying effect is responsible for some of the prejudice against saturated steam under pressure because of the mistaken idea that all steam above 100° can dry the wool and reduce fixation. Elaborate precautions to make sure the steam is saturated [7] would not be necessary, as it is most unlikely that steam in the average mill steam line would be anything but saturated.

TABLE X. Effect of Superheated Steam and Other Methods of Heating on Dye Fixation

Dye, 4.4% Cibalan Black BGL (4% wt./vol. in paste); solvent, 40% ethanol

Heating method	Dye fixed, %, after 10 min.	30 min.	50 min.
Saturated steam, 3 lb./sq. in., 105° C.	57	82	85
Superheated steam, 0 lb./sq. in., 115° C.*	0	—	7
Metal bath, 105° C.	42	56	67
Oven, 75° C.†	1	0	1

* Thermometer in contact with wool registered 105° C.
† Solvent, butanol 10%, oven saturated with water and butanol vapor.

TABLE XI. Steaming Times at Different Pressures for Fixation of Various Dyes

Composition of printing paste:

Dye	20–80	g./l.
Acetic acid (glacial)	30	ml./l.
Thickener (Solvitose H4M)	40	g./l.
Benzyl alcohol	50–100	ml./l.*
Water	QS. 1	l.

* Quantity depends on amount of dye; 30 ml./l. for chrome dyes. For the latter, chromium fluoride 30–60 g./l. and Neovadine AN 5 ml./l. also added.

Pressure, lb./sq. in.	Temperature, ° C.	Time (min.) for Premetallized and acid dyes: Light shades 20–30 g./l.	Black 80 g./l.	Chrome dyes 20–80 g./l.
0	100	40–50	100–120	—
3	105	12	35	60–90
5	108	10	25	40–50
7	111	8	20	30–40
10	115	6	12	23–30
15	121	4	7	10–15
20	126	3	4	5–10
30	135	2	2	2–3

Figure 9 gives typical results for a heavy shade of a premetallized dye, showing the effect of an increase in the steam pressure on the rate of dye fixation. It can be seen that substantial increases in the rates resulted from increases in the steam pressure. Of course, with a light shade the effect was less marked. It is not suggested that the pressure increased the rate of fixation, but rather that the simultaneous increase in temperature was responsible. Figure 9 also shows the increases in rate due to the use of solvent. On its own, altering the steam pressure had no appreciable effect on depth of color of premetallized dyes, although there was some evidence of improvement with chrome dyes.

The rates of fixation of a number of the dyes listed in Table VIII and Figure 6 were determined at different pressures with benzyl alcohol in the paste. Table XI shows the approximate time required to obtain satisfactory fixation (90–95%) of most of the dyes using the modified paste recipe shown.

For a batch process it would not be practical to use pressures above 10–15 lb./sq. in. because of the long warming-up periods for large steaming chambers (15 min. or more); also the margin of safety between dye fixation and yellowing became less as the pressure was increased (compare with Table V).

The practice of operating steaming chambers with large quantities of steam escaping is not to be recommended when using solvent, as this could reduce the rate by premature loss of solvent. The container used in this work for steaming at atmospheric pressure allowed a greater amount of steam to escape than the pressure steamer, so that loss of solvent at atmospheric pressure was probably responsible for the great difference between the "with solvent" curves for 0 and 3 lb./sq. in. in Figure 9.

Mill Trials

Several mill trials were undertaken, using the conditions shown in Table XI, with a chrome black and

premetallized black, grey, and brown. As the steaming chamber was not specifically designed for high pressure operation, the highest pressure which could be safely used was 7 lb./sq. in. This was high enough for the light shades, but a higher pressure would have been preferable for the blacks. At this pressure, the premetallized grey and brown were steamed 8 min., the black 20 min., and the chrome black 35 min. after the steaming chamber reached operating temperature.

For all, fixation was at least 95%, and depth of color was superior to that obtained by the conventional method. The increase in depth of color would be a distinct advantage with black, but may cause difficulties when matching other shades previously printed with a conventional recipe. However, once a shade was established with the modified paste, its reproducibility would be much easier, because wetting and penetration of the sliver would always be more even and complete. During mill trials two slivers printed on separate occasions with the same conventional paste recipe had 1.5% and 2.5% of dye deposited on the wool. Variations of this order were never observed with paste containing solvent.

The warming-up time of the chamber was about 20 min. Obviously some dye fixation would occur in this time, so that some sliver was removed at the end of the warming-up period. With the premetallized black, 55% of the dye was fixed, and with the grey, 93%. Therefore, the times in Table XI could be reduced, but this would have to be determined for individual steamers.

To determine whether size of the sliver bundle had any effect, bundles of various sizes wrapped in canvas covers were steamed. It was found that fixation and (for chrome dyes) development of color was better on the inside than the outside with even the largest bundle. For example, with the premetallized black, fixation was 91% on the extreme surface and 98% throughout the rest of the bundle. Therefore, it is apparent that the steam could readily penetrate even large bundles, and the larger the bundle the better from the point of view of fixation and development of color. Underdevelopment of chrome dyes on the surface of the bundle was prevented by the use of wet covers as described above.

Microscopic examination of cross sections of fibers printed during mill trials with Cibalan Black BGL (80 g./l. in paste) using both the conventional method (no solvent, 2 hr. steaming at 3 lb./sq. in.) and the method developed here (10% benzyl alcohol, 20 min. steaming at 7 lb./sq. in.) showed that the latter gave more even distribution of dye from fiber to fiber and greater penetration of dye into each fiber. A similar effect has been reported [10] when dyeing in the presence of amyl alcohol. The greater depth of color obtained with the modified method could be attributed to this effect.

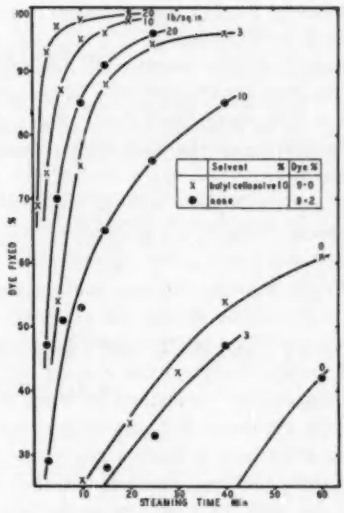

Fig. 9. Effect of steam pressure on rate of fixation of Cibalan Black BGL (8% wt./vol. in paste). Pressure marked on curves in lb./sq. in.

Summary

The inclusion of suitable solvents in the printing paste greatly increased the rate of dye fixation and depth of color. Benzyl alcohol was chosen as the most suitable solvent for commercial use.

Increasing the steam pressure also gave substantial increases in the rate of fixation when the steam was saturated; superheated steam reduced fixation by its drying effect.

Acetic acid was used in the printing paste because it was volatile and reduced the pH of the unprinted part of the sliver during steaming so that yellowing was retarded until well after the dye was fixed. Steaming at high pressures for times required to fix dyes with the slowest rates did not alter fiber breaking strength.

Neutral dyeing premetallized and many acid dyes gave particularly good results in the presence of sol-

vent. Increasing the dye concentration increased the time required for fixation.

Pretreatment of the wool with alcoholic KOH increased the rate appreciably only in the absence of solvent or at low steam pressures. Solvent extraction or acidification of the wool before printing had no effect on the rate.

Neither the thickener, several anionic wetting agents, sodium chlorate, nor glycerol (common paste constituents) had much effect on rate of fixation.

Hygroscopic solvents did not prevent the reduction in rate caused by drying the printed sliver before steaming. Wrapping the sliver bundle with wet cloths was more effective in this respect.

The modified paste developed as a result of this work and the recommended steaming times for different dyes at various pressures are given in Table XI. The time required depends on the type and amount of dye and the steam pressure, but in most cases dye fixation could be achieved in a matter of minutes instead of the usually accepted 1 or 2 hr.

Microscopic examination of fibers showed that the new technique gives better penetration and distribution of dye than former methods. A number of mill trials have shown that the method can be applied successfully on the commercial scale, and it is now being used commercially in Australia.

Acknowledgments

The author wishes to thank Dr. M. Lipson and Dr. C. H. Nicholls for a number of helpful discussions, and Mr. H. D. Feldtman for valuable assistance with the experimental work. Appreciation is also recorded of the cooperation and assistance of the management and staff of the Returned Soldiers and Sailors' Woolen Mill, Geelong, where the mill trials were conducted.

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Manuscript received April 15, 1957.

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the Journal. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the Journal is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Microscopic Observations on Cotton Fibers Subjected to Enzymatic Degradation

Crops Research Division
Agricultural Research Service
U. S. Dept. of Agriculture
Beltsville, Maryland
June 24, 1957

To the Editor
Textile Research Journal

Dear Sir:

In 1952, Blum and Stahl [2] published an interesting paper on the enzymatic degradation of cellulose fibers in this journal. The present communication is closely related in subject matter to the section of these authors' paper which is sub-titled "Microscopic Observations," and describes certain experimental results which are considered to be in no way contradictory to theirs but rather supplementary in nature.

In their opening paragraph, Blum and Stahl noted the existence of indirect evidence suggesting that the microbial degradation of cotton fiber is to a large extent a localized process. They then proceeded to define the main problem of their investigation in these words: "The fundamental question immediately follows: In which region or regions of the fiber does the destructive attack occur?" A major part of their report concerns experiments in which cotton fibers were subjected to the action of filtrates from the growth of the fungus *Myrothecium verrucaria 1334.2* and then examined microscopically after swelling in cuprien. In describing their observations, they write, "The most striking result of degradation was the appearance of one or two prominent spiral lines which appeared as spiral fissures as swelling proceeded to its limit . . . In highly degraded fibers . . . the fissures in some cases extended to the lumen, and the fiber on swelling opened into a ribbon similar to an untwisted drinking straw . . . Also in the highly degraded specimens shallower notches could be seen on the surface of the fibers . . ."

In certain experiments in this laboratory, cotton fiber has been exposed to the action of filtrates from the growth of the above-mentioned *M. verrucaria 1334.2;* instead of helical fissures such as were observed by Blum and Stahl there occurred principally very striking transverse cracks and complete transverse breakage or fragmentation of the fiber. An essential difference between our experiments and those of Blum and Stahl was that in our case the fiber was *shaken* in the filtrate. Apparently the enzyme may injure the fiber in the transverse plane, and the bending action incident to shaking then causes the fiber to snap apart at the weakened point.

In these experiments, 5 cc. of *Myrothecium* filtrate, prepared from a growth of the fungus on raw cotton in the presence of a mineral salts solution (exactly as described for the preparation of S-factor in 500 cc. Erlenmeyer flasks [7], p. 879), was added to 10 mg. of raw cotton in a 60 cc. bottle and the suspension agitated moderately on a laboratory shaker at 20° C. for 2 hr. At the end of this time

it could be seen upon holding the bottle toward the light that there were many small fragments in the liquid; these were noted under the microscope to be short sections of fiber, varying in length principally from about 10 to 100 times the fiber's width. The broken ends were almost all very sharp in outline and at right angles or nearly at right angles to the main fiber axis, *not* helical in direction. The photomicrographs in Figure 1 illustrate the appearance of the material. It should be noted that all fibers shown in the photomicrographs here were mounted in water, not swollen in cuprien as were fibers shown by Blum and Stahl [2].

The percentage of the fiber fragmented in experiments of the above type was estimated by washing out the fragments from the residual fiber mass with a gentle stream of water and drying and weighing the latter; the percentage fragmented was thus found to be in the range of 20–30% of the original fiber. A control sample of fiber shaken in mineral salts solution exhibited no fragmentation and few, if any, transverse marks in addition to the small number visible in the original sample. Another type of control, fiber incubated with filtrate but without shaking, showed almost no fragmentation. A filtrate from the growth of *Chaetomium globosum 1042.4,* prepared in the same manner as the *Myrothecium* filtrate, was quite as active in causing fragmentation; the microscopic appearance of the fiber was also similar. In enzyme exposures of this type, the tendency to break at any weakened point is presumed to be related not only to the degree of weakening but also to the amount of leverage exerted at the point of weakness. For this reason the cracking of the fiber becomes progressively more difficult as it becomes more and more fragmented. There was some thought that possibly zones of enzymatic susceptibility might occur at points of reversal, but examination of cracked and fragmented fiber with a polarizing microscope failed to yield support for this idea.

Although helical cracking occurred to a very minor extent in our first experiment, described above, it was obviously a very secondary feature in comparison with the large amount of transverse cracking and fragmentation. A simple means was found, however, by which a very major amount of helical splitting, presumably essentially the same as Blum and Stahl's "spiral fissures," could be obtained with a very short period of exposure of fiber to enzyme. The process utilized undried fiber, i.e., fiber which had been taken from a relatively mature but unopened cotton boll and not allowed to dry before exposure to the filtrate. This result was obtained by placing a small amount of undried fiber (about 25 mg. wet weight) into 5 cc. of filtrate and shaking for 1 hr. There resulted a very large amount of conspicuous helical cleavage, often extending completely

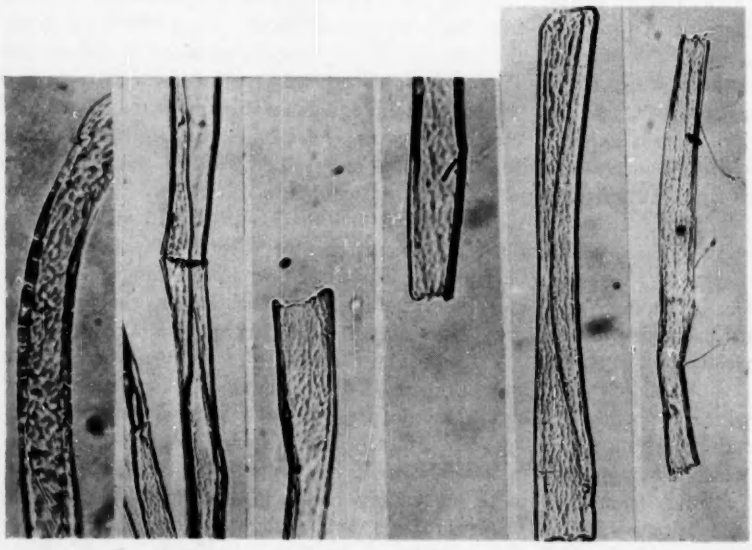

Fig. 1. Photos showing transverse cracking and breaking of cotton fibers as seen after 2 hr. of exposure, with shaking, to filtrate from *Myrothecium verrucaria.* (*A*) and (*B*) cracks in fiber; (*C*) and (*D*) broken ends of fragments; (*E*) and (*F*) whole fragments. Magnification approximately 200× for *F* and 400× for other photos.

through the secondary wall. The appearance of this material is illustrated in Figure 2.

Transverse cracking has been observed before in cotton fibers, but apparently not in clearly proven causal association with micro-organisms or enzymatic action. Clegg [4] has figured many instances of transverse cracking and fragmentation in worn cotton textiles. Her figures and statements leave no doubt about the transverse nature of the cracks observed, as distinct from spiral or helical splitting. She states, for example (p. 122), "Figure 22 depicts a cotton fibre stained to show the slow spiral of the cuticle and the quick spiral of the secondary cellulose is also seen. The stained fissure cuts across both spirals, obviously bearing no structural relation to either. . . ." She uses the designation "transverse cracking" [4] which we follow here. It is true that Blum and Stahl do write of "surface notches" and "secondary notches," but they do not mention a deep cracking or transverse segmentation of the fibers. The only good example of transverse cracking associated with microbial action which the writer has seen in the literature is that figured by Fleming and Thaysen in 1920 [5]. In this case the fibers were apparently not of accurately known history; one wonders whether it is possible to be really certain of the cause of the cracking. Abrams [1] incubated cotton fiber for short periods with *Chaetomium globosum* and observed the appearance of "holes" in such fiber when subsequently treated with NaOH. His alkali-soluble areas may be related to the transverse cracks noted in our work. In contrast to transverse cracking, helical cracking has been observed before by Blum and Stahl [2] with both enzyme-exposed and fungus-incubated fiber and by Clegg [3] in naturally-infested raw cotton.

Helical and transverse cleavage in our experiments are quite different in microscopic appearance. One might assume that they involve fundamentally different types of chemical action, the former a separation of cellulose chains and the latter perhaps a breaking of cellulose chains. Superficially these two types of action appear to correspond to the functions attributed by Siu and Reese [9] to their cellulolytic enzymes C_1 and C_x respectively. The comparison, however, does not seem to bear further analysis, since these authors postulate that enzymatic degradation of native cellulose involves the action of C_1 (separating chains) as a necessary antecedent to that of C_x (breaking chains), whereas our transverse

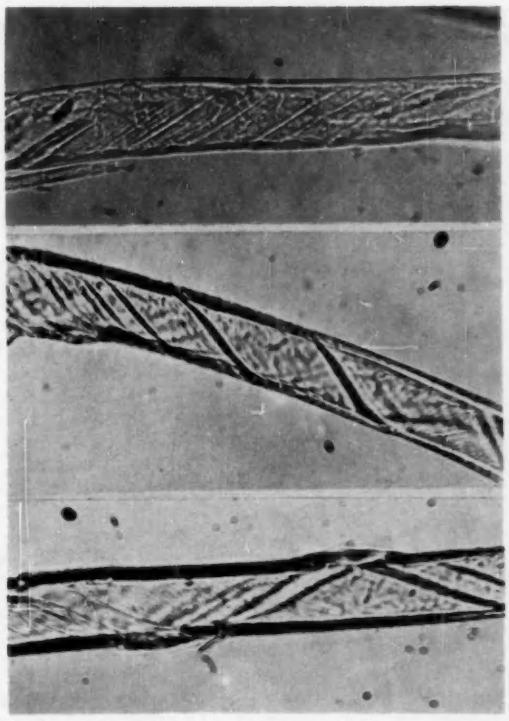

Fig. 2. Cotton fibers exhibiting helical splitting after 1 hr. of exposure to filtrate from the growth of the fungus *Myrothecium verrucaria*. These fibers had been taken from a relatively mature cotton boll before its natural opening and then exposed to the filtrate without prior drying of the fiber.

cleavage, here described, is obviously not dependent upon prior helical cracking. This is not to say that such a sequence, i.e., helical cleavage followed by transverse, does not occur. As a matter of fact, the ragged appearance of a fiber highly degraded by a fungus may be a result of action in helical, transverse, and other directions. Still, transverse action is not dependent on prior helical action.

Why did the undried fiber develop such a very great amount of helical splitting, and develop it so rapidly, in our experiments? The writer's present interpretation is that in undried fiber the helically arranged cellulose molecules are relatively far apart from each other, so that the large enzyme molecule can get between them more readily than in a dried fiber, in which the chains are much closer. When incubated on undried cotton in the boll as described in previous work on fluorescence [8], the fungus *Aspergillus flavus* also produces much helical split-

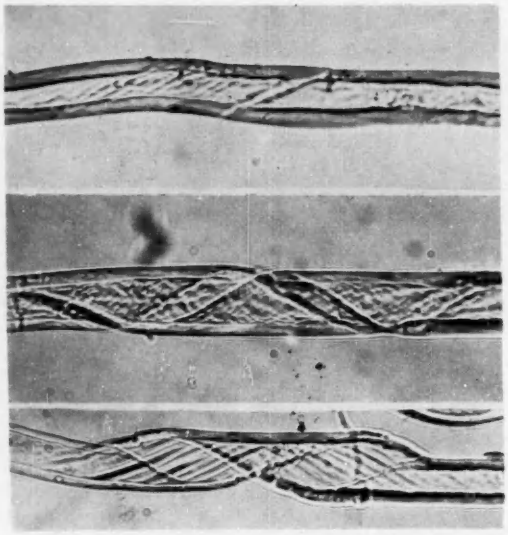

Fig. 3. Cotton fibers from a boll naturally infected in the field at the time of boll opening by the fungus *Diplodia gossypina*. Note helical direction of cleavage. Gross appearance of a boll of the type from which this fiber was taken has been figured before ([6] Figure 1).

ting. Helical splitting is also common in cotton which has been attacked by micro-organisms in the field before the fiber has dried (see Figure 3).

A colleague has suggested the possibility that sites at which transverse breakage occurred in our shaken-with-enzyme fiber (Figure 1) might actually be points at which there was already prior mechanical damage which had occurred during ginning. The fiber of Figure 1 had been ginned on a small hand laboratory roller gin which is quite gentle in its action; further, the same sort of transverse breakage by the enzyme has been observed with fiber which has been removed from the seed by hand. In all cases the fiber had been taken from plants in the field about 24 hr. after the bolls had opened and no artificial heat had been applied to it. It therefore seems rather improbable to the writer that transverse breakage by the enzyme is dependent upon prior damage of the fiber as a result of mechanical action, heat, or light.

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PAUL B. MARSH
Physiologist

The Reactivity of the Disulfide Bonds of Stretched Wool Fibers

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Wool Textile Research
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Australia
July 25, 1957

To the Editor
Textile Research Journal

Dear Sir:

On the basis of qualitative physical observations, Astbury and Street [1] and Speakman [6] have suggested that the disulfide bonds of stretched wool are more reactive than those of unstretched wool. However, two previous attempts to demonstrate this by quantitative chemical analysis have failed to detect any effect of stretching on disulfide reactivity [2, 4], but both of these experiments involved extensions of only 30%, which would convert only a fraction of the α- to β-keratin. We have accordingly investigated the effect of 90% extension of fibers on the extent of reduction of disulfide bonds by thioglycollate solutions.

Bundles of fibers from a single lock of wool (10 cm. long, weight ca. 0.1 g.) with their ends set in blocks of Epikote resin (Shell Chemicals Ltd.) were prepared, using Lincoln wool. One such bundle was left overnight under load in a 0.5 *M* sodium thioglycollate solution at pH 5.0 so that it eventually extended by 90%; a similar fiber bundle was left unstretched in the same solution. From previous work [5] it is known that these are equilibrium conditions; hence we are not concerned with rates of reaction. The thioglycollate solution was run off; after the reduced fibers were washed with water, they were treated with iodoacetamide solution at pH 9 to convert the cysteine side chains to S-carbamylmethyl cysteine groups. After washing, the fibers were conditioned and hydrolyzed and the cystine content of the hydrolysate estimated by amperometric titration [7]. The results of a duplicate experiment of this kind are recorded in Table I.

TABLE I

Treatment	% cystine on dry weight
(Untreated wool)	(10.0)
Unstretched wool, reduced and coupled with ICH_2CONH_2	5.6, 5.3
Stretched (90%) wool, reduced and coupled with ICH_2CONH_2	4.1, 4.1

These results show that the residual cystine content of the stretched fibers is less than that of the unstretched fibers; i.e., the reduction of the cystine has proceeded further in the case of the stretched fibers.

Stretching a wool fiber theoretically could be expected to affect the reactivity of disulfide bonds in either of two ways: (1) part of the energy of stretching could cause strain in bonds causing a lowering of the activation energy necessary to break them, or (2) the change in configuration from α- to β-keratin might alter the environmental factors governing the extent of the reaction. The present experiment considered alone does not permit an unequivocal decision to be made between these hypotheses. However, the first suggestion implies an effect on the reaction rate rather than on the equilibrium value of the reaction. Hence it should have been observed in the earlier experiments of Lindley & Phillips [4] on the action of alkalis on stretched wool, especially as the strain required to produce 30% extension of a wool fiber is not very different from the strain required for 90% extension of a reduced fiber [3]. We prefer therefore to interpret the result as being due to configurational (and hence environmental) changes in the keratin structure. The result can thus be regarded as reinforcing the analogy between stretched wool (β-keratin) and denatured proteins.

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J. P. E. Human
H. Lindley

Correction—Brenner and Scocca Article

Johnson & Johnson
New Brunswick, N. J.
June 20, 1957

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

A number of typographical errors appeared in the paper "The Prediction of the Micronaire Value for a Bale or a Group of Bales—A Statistical Study" by Brenner and Scocca, **26**, 899–902 (1956):

1. Table IV, $|\bar{X}_{\bar{2}} - \bar{X}|_{\bar{6}}$ in the column headed Maximum Difference should read $|\bar{X}_{\bar{2}} - \bar{X}_{\bar{6}}|$.
2. Page 901, first column, fourth line from bottom, $X_{\bar{2}}$ should read $\bar{X}_{\bar{2}}$.
3. Page 901, second column, the equation in III.2 reads $N^{\frac{1}{2}}$ and should read $N^{-\frac{1}{2}}$, and σ should be s.
4. Page 901, second column, last line, the minus sign in the denominator should be plus and σ should be s.
5. Page 902, first column, line 11 $|\bar{X}_{\bar{2}} - \bar{X}_{6}|$ should read $|\bar{X}_{\bar{2}} - \bar{X}_{\bar{6}}|$.

The following editorial changes were suggested by several readers. It should be emphasized the paper reports findings in two different experiments. The data reported in Table I were determined by the best techniques known to the authors; the micronaire values were determined on carefully cleaned, opened, and conditioned samples. The calibration of the Micronaire was checked after every second determination. The conclusions derived from these data are reported in Table II. These results are primarily of interest to research workers.

The data in Table III and the following tables apply to a practical experiment. The $X_{\bar{2}}$ values were determined by a cotton classer following his usual routine. This procedure is less likely to give as precise a prediction as the procedure used to obtain the data in Table I. The standard deviation of the difference $X_{\bar{2}} - X_{\bar{6}}$ is expected to be larger than that fround for the data in Table I as they were, being 0.393 and 0.139, respectively.

In Table II the figures under the column headed 99% were erroneously reported; 18 (17.4) should read 14 (13.2), 5 (4.3) should read 4 (3.3), and 2 (1.9) should read 2 (1.5).

On page 902, first column, line 2, delete words following "to ensure" through the first sentence in the next paragraph. Replace with "with confidence coefficient $1 - \alpha$ that the two bales have mean micronaire values which differ by an amount included in the interval

$$\bar{X}_1 - \bar{X}_2 \pm \zeta_{\left(1-\frac{\alpha}{2}\right)}\sigma\sqrt{\frac{1}{N_1} + \frac{1}{N_2}}$$

For fixed $N_1 + N_2$, it can be shown that $1/N_1 + 1/N_2$ has its minimum when $N_1 = N_2$."

In IV. Conclusions, paragraph 2 should read "2. To predict the true mean of a bale within 0.1 micronaire value, with confidence coefficient 0.95, eight random samples are required (Table II)."

F. C. BRENNER